Photopolymerization of Vinyl Chloride by Mercury Sensitization

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A. Introduction

In the course of the study of photopolymerization of vinyl compounds, we have found that the polymerization of vinyl chloride (in the vapor phase) initiated by the light of a low pressure mercury lamp, is mainly a photosensitized reaction by mercury vapor and that the effective light is 1850 Å and not 2537 Å. The present paper will report the main features of the reaction and some kinetic studies about it.

B. Apparatus and Procedure

The main part of the apparatus ordinarily used is shown in Fig. 1. It is somewhat similar to the one used by H. W. Melville[1]. B is the reaction vessel of about 20cc. (quartz) and A is a mercury-cut through which the sample is led into the reaction vessel, which is also utilized as a manometer to trace the reaction. The temperature was usually controlled by streaming water. The mercury lamp is a simple D. C. type of about 20 cm. long (300 W).

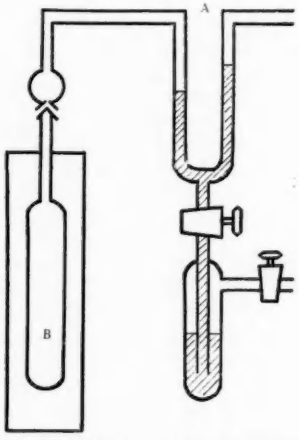

Fig. 1 The main part of the apparatus

C. Some Features of the Reaction

1. When the illumination is commenced, the pressure begins to decrease and a white polymer is deposited on the surface of the vessel. The deposition is observed only on the front part, and when the vessel is covered by Al foil partly, the back side of the covered part is completely free from the deposit, the boundary being as sharp as the foil itself. There is no sign of any side reactions.

2. When the illumination is cut off, the reaction stops at once, showing that there is no active material surviving such as observed by Melville in the case of methyl metacrylate[1]

3. When the wall of the vessel is lined with the material transparent down to 2000Å such as NaCl or paraffin, the reaction is affected remarkably. When pieces of metal such as steel or bronz are previously thrown into the vessel, the rate is slightly increased while pieces of quartz rods of the same origin as that of the vessel slightly retards the rate.

4. When only the light 2537 Å is employed, the reaction scarcely goes on. This fact was particularly confirmed by the following experiment. Using the reaction vessel with two parallel plates, it was ascertained that the intensity of light 2537 Å which had passed through the reaction vessel was quite strong and yet there was observed no pressure decrease nor the white deposit on the wall of the vessel. On the other hand, when the light of mercury lamp was filtered by a thick layer of water, the reaction was often suppressed remarkably. These facts strongly suggest that the effective light is the one of such short wave length that is liable to be absorbed by a trace of impurity in water.

5. When mercury vapor is cautiously eliminated, the reaction is reduced to a very small quantity. This fact was confirmed by the apparatus particularly designed, the pressure decrease being measured with a membrane manometer.

All the above facts strongly support the view that the present photopolymerization is initiated by 1850 Å line of Hg lamp, the intensity of which is so weak that it is almost completely absorbed in the region near the front part of the vessel and that the reaction is heterogeneous taking place on the wall of the vessel at least in some steps of the overall reaction. In addition, the mercury vapor supposedly acts as photosensitizer.

1) H. W. Melville, *Proc. Roy. Soc.*, **A163**, 511 (1938); *Proc. Roy. Soc.*, **A167**, 99 (1937).

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D. Some Kinetic Studies

1. The Effect of the Pressure of Vinyl Chloride—In the present experimental condition, the pressure decrease is very small compared with the initial pressure of vinyl chloride, and it goes on linearly against time.

The pressure decrease during initial 60 minutes is completely proportional to the initial pressure of vinyl chloride showing that the reaction is of the first order with regards vinyl chloride. (See Fig. 2)

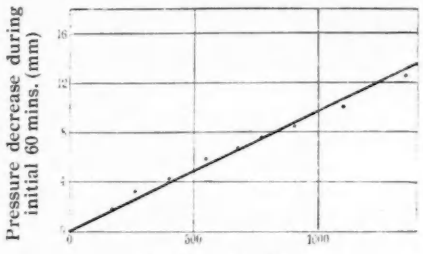

Fig. 2. Dependence of the rate upon the pressure of vinyl chloride

2. The Effect of Light Intensity—The reaction rate is proportional to the intensity of light as shown in the following table.

THE EFFECT OF INTENSITY OF LIGHT UPON THE RATE

	P (Press. of CH_2=CHCl)	I (Relative intensity)	ΔP (Press. decrease per hr.)	k' ($\Delta P/P$)	k'/I
1	760.5 mm	1	9.5 mm	0.0125	0.0125
2	763.0	1/2	5.2	0.0068	0.0136
3	768.0	1/3	3.4	0.0044	0.0132
4	761.2	1/4	2.4	0.0032	0.0128

In this experiment the intensity of light was varied with the use of blackened copper nets or black perforated celluloid plates.

3. The Effect of Temperature—The reaction rate was measured at three temperatures 10°C, 41°C and 95°C. At all temperatures, the pressure decrease is linear against time, and the reaction rate calculated from the slope of each line is proportional to the pressure of vinyl chloride.

Under the present experimental condition, the rates at various temperatures are expressed by the following formulas.

10°C $v=0.00017\ P_{C_2H_3Cl}$ (mm./min.)

41°C $v=0.000025\ P_{C_2H_3Cl}$

95°C $v=0.00001\ P_{C_2H_3Cl}$

The measurement at 95°C is somewhat unreliable but it is evident that the rate decreases with the rise of temperature. The activation energy is calculated to be about −6 Kcal.

4. The Effect of the Pressure of Mercury Vapor—The effect of the pressure of mercury vapor was examined by comparing the results of the two series of experiment at elevated temperatures of which the one was performed in the presence of a mercury drop at the bottom of the vessel while the other was done in the ordinary condition. The result is that the rate increases monotonously with the rise of the pressure of mercury vapor as shown in the following table (mean value of several experiments).

Temp.	Mercury pressure	Rate of pressure decrease
	mm.	mm./min.
41 °C	0.0005	0.000025
	0.0065	0.00025
95 °C	0.0005	0.000007
	0.21	0.0014

The rate may be regarded as approximately proportional to the mercury pressure in its low pressure region.

To sum up the above results, the reaction rate can be expressed as follows.

$$v=k\ [CH_2=CHCl]\ [Hg]\ I \qquad (1)$$

where I is the intensity of the incident light, which is absorbed completely.

E. Discrimination of the Function of Mercury Vapour on the Basis of the Photopolymerization by Al Spark

In section C, it was shown that the existence of mercury vapor is essential for the reaction.

To decide whether the function of mercury is sensitization or catalysis, the investigation of photopolymerization induced by the light of different wave length other than 1850 Å is expected to be much helpful. Thus if the polymerization takes place by another light and the accelerating action of mercury vapor is still perceived, then the function of mercury vapour in the case of mercury lamp would perhaps be catalytic in nature, while on other hand, if no effect of mercury vapour is existent in the case of another light, the action of

mercury in the case of mercury lamp ought to be a sensitizing one.

From such a viewpoint, we examined the photopolymerization by Al spark and particularly the effect of mercury vapour on the reaction rate. The conditions of Al spark employed are as follows: spark gap 0.5 cm., voltage 10000 V; condenser inserted; capacity, 0.02 μF. By taking the emission spectrum, three strong lines near 1850 Å were confirmed to exist in this condition. We were much indebted to Dr. T. Kuzirai of Kyoto University for taking the spectrum.

1. The polymerization occurs in the ordinary condition (mercury vapour is existent) just in the same order of magnitude as in the case of mercury lamp.
2. The polymer deposited is quite different in appearance from that obtained in the case of mercury lamp. It is transparent and looks like liquid. Even when mercury vapour is excluded as cautiously as possible, the reaction rate is not influenced beyond the experimental error. It seems rather to be accelerated to some extent.

The above results lead us to the conclusion that the polymerization by Al spark is quite a different reaction from that by mercury lamp, and that in the former case it is a simple photochemical one, while in the latter it is a photosensitized reaction by mercury vapor.

F. Discussion of the Mechanism on the Basis of Kinetic Formula

In Section D. the kinetic formula (1) was derived from the experimental results.

The reaction mechanism must be such as conforms to the above relation, and this condition gives us the criterion to decide the probable mechanism.

The problem is therefore to tabulate all the mechanisms conceivable and to give for each of them an appropriate reaction formula.

Let us therefore classify, at first, the types of reaction in the following way.

α) Complete homogeneous gaseous reaction

β) Heterogeneous reaction

β) is further classified into seven types according to the circumstances that each step of the overall reaction, that is initiation, propagation, and termination, be a gaseous or a wall reaction. They are

	β							α
	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)
Init.	W	W	W	W	G	G	G	G
Prop.	W	W	G	G	W	W	G	G
Term.	W	G	W	G	W	G	W	G

In the above list, G and W means a gaseous or wall reaction, respectively. All these types must be further classified according to the detailed scheme of initiation, propagation and termination.

Case (α) Let us first consider case (α). To derive an overall kinetic formula, one must give the rate expression for each step.

I) Initiation

$$Hg+h\nu \rightarrow Hg^* \quad Hg^*+M \rightarrow M^*+Hg$$

The velocity of initiation is given by the following equation.

$$v_i = k_i I \frac{\alpha_{Hg}[Hg]}{\alpha_M[M]+\alpha_{Hg}[Hg]}[M]$$

where I is the intensity of light to be absorbed, α_{Hg} and α_M are the molecular extinction coefficients of mercury and vinyl chloride vapour respectively. The above equation is derived on the assumption that the spontaneous deactivation of excited mercury atoms is not important.

The magnitude of α_{Hg} and α_M are unknown but there is no doubt that the vapor of vinyl chloride absorbs the light in the region of 1850 Å not so little. Besides $[M] \gg [Hg]$. Therefore, it may safely be assumed that $\alpha_M[M] \gg \alpha_{Hg}[Hg]$. This relation may also be supported to some extent by the experimental result. Thus if $\alpha_M[M] \approx \alpha_{Hg}[Hg]$ the reaction formula can not be so simple as (1). Again, if $\alpha_{Hg}[Hg] \gg \alpha_M[M]$, v_i ought to be independent of [Hg] and the overall reaction rate cannot be proportional to [Hg] irrespective of any scheme of the two succeeding steps, if the gaseous initiation really holds at all.

For these reasons, the above formula can be put as follows

$$v_i = k_i I \frac{\alpha_{Hg}[Hg]}{\alpha_M} \qquad (2)$$

II) Propagation

$$M^*+M \rightarrow M_2^* \quad M_2^*+M \rightarrow M_3^*$$

There may be no question as to the propagation process,

$$v = k_p[M][R]$$

where R is an active radical.

III) Termination

Types of termination conceivable are as follows.

a) R+R→P
b) R+Hg→P
c) R+M→P

Now the velocity of the overall reaction is given by v, that of the propagation process, and the application of the stationary state method easily leads to the following kinetic formulas for each case.

a) $v=k_p\sqrt{\dfrac{k_i}{k_t}\dfrac{I}{\alpha_M}\alpha_{Hg}}[Hg][M]$

b) $v=k_p\dfrac{k_i}{k_t}\dfrac{I}{\alpha_M}\alpha_{Hg}[M]$

c) $v=k_p\dfrac{k_i}{k_t}I\dfrac{\alpha_{Hg}}{\alpha_M}[Hg]$

All the above formulas contradict the experimental result. Thus the conclusion that the reaction is not homogeneous, can be derived merely from the kinetic formula.

Case (β) The analogous deduction can be made for case (β). The details of the discussion will be given eleswhere and only essential points will be described here briefly.

I) Initiation when the initiation takes place in the gaseous phase, the result is just the same as in the case α.

When the initiation takes place on the wall, v_i will be given by the following equation

$$v_i=k_i\,I\,\frac{\alpha_{Hg}[Hg][[M]]}{[M]} \qquad (3)$$

where [[M]] represents the surface concentration of vinyl chloride monomer.

This relation can be derived as follows.

Excited mercury atoms which can arrive at the wall during its life are those which exist in the extremely close neighbourhood of the surface. If the mean distance through which activated atoms can reach the wall be put as Δd, v_i may be put as follows:

$$v_i=k_i\,I\,\alpha_{Hg}[Hg]\,\Delta d\,[[M]]$$

Δd depends on various factors, but in the present case it is essential how it is influenced by the pressure of vinyl chloride. Taking account of the fact that the experimental relation (1) is very simple, it may be most probable to put Δd as inversely proportional to the latter, since it is theoretically expected to decrease as the pressure of vinyl chloride increases. Thus the equation 3) is obtained*.

Using 2) or 3) for initiation, the following possibilities were criticized for i), ii), iii), iv), v), vi), vii) of case (β).

I) Initiation Gas or wall

II) Propagation Radicals combine with monomer molecules (in the vapour phase) irrespective whether the reaction takes place in the gaseous phase or on the wall.

III) Termination Gas: Three possibilities similar to a), b), c) of (α)

Wall: d) [R]+[R]→[P]
e) [R]+R→[P]
f) [R]+Hg→[P]
g) [R]+M→[P]
h) [R]+[S]→[P]
i) [R]+[M]→[P]
j) R+[M]→[P]
k) R+[S]→[P]

where S means the wall of the vessel, and [ ] represents the molecular species in the adsorbed state.

The result of the critique is that five types of mechanisms conform the relation (1) and if one takes account of the fact that the addition of quartz rod decrease the rate to some extent, then the selected mechanisms are as follows.

	Init.	Prop.	Term.	Type of termination kinetic formula
v)	G	W	W	h) [R]+[S]→P $v=\dfrac{k_p k_i}{k_t} I \dfrac{\alpha_{Hg}}{\alpha_M}[Hg][M]$
				i) [R]+[M]→P $v=\dfrac{k_p k_i}{k_t} I \dfrac{\alpha_{Hg}}{\alpha_M}\dfrac{[Hg][M]}{[[M]]}$
Vii)	G	G	W	k) R+[S]→P $v=\dfrac{k_p k_i}{k_t} I \dfrac{\alpha_{Hg}}{\alpha_M}[Hg][M]$
				j) R+[M]→P $v=\dfrac{k_p k_i}{k_t} I \dfrac{\alpha_{Hg}}{\alpha_M}\dfrac{[Hg][M]}{[[M]]}$

It is to be noted that the adsorption of vinyl chloride must be saturated in order that the scheme v) i) and vii) j) may be adopted.

The conclusion is that the mechanism of the principal polymerization reaction by mercury lamp is given as follows.

Initiation takes place in the gaseous phase

* Any relations other than (3) can not lead to (1), how the succeeding steps may be assumed.

Propagation proceed in the gaseous phase or on the wall. Termination takes place on the wall and the radical in the gaseous phase is stabilized either by its collision against the surface or by the interaction with adsorbed monomer molecules, while in the case that propagation proceeds on the wall, the radical is stabilized spontaneously or by the interaction with adsorbed monomer.

Thus the scheme of the reaction is given as follows.

Init. $Hg + h\nu \rightarrow Hg^*$
$Hg^* + M \rightarrow M^*$

Prop $M^* + M \rightarrow M_2$
or $M^* \rightarrow [M^*]$
$[M^*] + M \rightarrow [M_2^*]$

Term. $[R] + [S] \rightarrow P$
or $[R] + [M] \rightarrow P$
or $R + [S] \rightarrow P$
or $R + [M] \rightarrow P$

Summary

It was found that the photopolymerization of vinyl chloride in the presence of mercury vapor is mainly a sensitized reaction due to the latter. The effective light is 1850 Å and not 2537 Å.

As a result of some kinetic studies, it was confirmed that the initiation of the chain takes place in the gaseous phase, the propagation proceeds in the gaseous phase or on the wall, and lastly, the termination occurs only on the wall of the vessel.

Details of the experiment and full discussions will be published in Journ. Polytech. Osaka City University.

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Studies on the Organic Phosphorescence. I.

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Introduction

According to the current interpretation of the organic phosphorescence[1] which is emitted by many unsaturated compounds under suitable conditions, such as in solid solution or in adsorbed state, the whole process of phosphorescence concerns mainly the isolated molecule, and the phosphorescent state is a triplet state (T-state).

Now, the triplet state, which is considered to be of a biradical nature, deserves special attention from the photochemical standpoint[2] owing to its reactivity and especially to its extraordinary long life compared with the ordinary excited state (S′-state). But the role of the triplet state in connection with the photochemical reaction is not quite certain as yet, and the systematic studies are very much desirable.

The present authors have constructed an apparatus for the accurate measurement of decay of organic phosphorescence and are attacking the above problems by studying the quenching effects of many substances upon the phosphorescence, and especially are trying to determine whether quenchers affect on S′-state or T-state. The purpose of the present paper is to give some mathematical relations which may help to elucidate the mechanism of the quenching action, and to report some results as to the self-quenching (concentration quenching) of filter paper-Trypaflavine phosphor.

A. Kinetic Expressions for the Initial Intensity and the Life of Phosphorescence

From the standpoint of photochemistry, it may be essential to decide whether the quenching action operates selectively on the singlet S′-state or triplet T-state or alternatively on both states equally well. We considered about this problem on the basis of Lewis' scheme and arrived at the conclusion that the measurement of both the initial intensity and the life of phosphorescence in the absence and in the presence of quenching materials, may be much helpful for this decision. The mathematical procedure will be stated briefly below.

Lewis' scheme of phosphorescence is schematically represented as follows. (cf. Fig. 1)

* Physicochemical Studies of Organic Dyestuffs in Relation to Photochemistry V.

1) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944); G. N. Lewis, M. Calvin and M. Kasha, *J. Chem. Phys.*, **17**, 804 (1949).

2) M. Calvin and G. D. Dorough, *J. Am. Chem. Soc.*, **70**, 699; **71**, 4024 (1949).

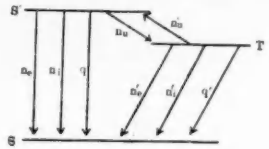


Fig. 1

1) S→S': excitation by light absorption.
2) Fluorescence is the emission accompanied when the molecule excited by the process (1) directly falls down to S-state.
3) S'→T: transition to the triplet state.
4) β-phosphorerescence is the emission which is accompanied with the transition T→S.
5) α-phosphorescence is the emission accompanied with S'→S which succeeds the process T→S'.

Put the various transition probabilities as follows.

From S'

n_e: transition to the ground state accompanied with the emission

n_i: transition due to inner quenching effect (including the effect due to the interaction between adsorbent and dye molecule. The effect of inevitable impurity may also be included)

q: quenching effect of a substance

n_u: transition to the triplet state

From T

n_e': transition to the ground state accompanied with the emission

n_i': transition due to inner quenching effect (analogous to n_i)

q': quenching effect of a substance

n_u': transition to S'-state

Using these constants, the differential equations for the number of molecules in S'-state (N_S) and in T-state (N_T), after the interruption of illumination are given as follows:

$$\frac{dN_S}{dt} = -(n_s + n_i + n_u + q)\, N_S + n_u'\, N_T \qquad (1)$$

$$\frac{dN_T}{dt} = -(n_e' + n_i' + n_u' + q')\, N_T + n_u\, N_S \qquad (2)$$

If we take account of the fact that the life time of S'-state is $10^{-7}\sim10^{-8}$ sec, while that of triplet T-state is of the order of 0.1 sec, the exact solutions which consist of the exponential terms can be approximately expressed by a single exponential term. Thus N_T and N_S after the interruption of illumination are given as follows.

$$N_T = \frac{n_u\, Q}{\pi_s \pi_t - n_u n_u'} \cdot e^{-\left\{\pi_t - \frac{n_u n_u'}{\pi_s}\right\} t} \qquad (3)$$

$$N_S = \frac{n_u\, Q}{\pi_s \pi_t - n_u n_u'} \cdot \frac{n_u'}{\pi_s} e^{-\left\{\pi_t - \frac{n_u n_u'}{\pi_s}\right\} t} \qquad (4)$$

where Q is the number of molecules excited per second during illumination, and

$$\pi_s = n_e + n_i + n_u + q$$
$$\pi_t = n_e' + n_i' + n_u' + q'$$

From (3) and (4) the intensity of phosphorescence at an arbitrary time (t) is given as follows.

$$I_p = n_e' N_T + n_e N_S = \frac{Q\, n_u}{\pi_s \pi_t - n_u n_u'} \left[n_e' + \frac{n_u' n_e}{\pi_s} \right] e^{-\left\{\pi_t - \frac{n_u n_u'}{\pi_s}\right\} t} \qquad (5)$$

The formula (5) gives the decay constant α (reciprocal of the average life τ, $\alpha = \frac{1}{\tau}$) and the initial intensity of phosphorescence as follows.

$$\alpha = \pi_t - \frac{n_u n_u'}{\pi_s} = (n_e' + n_i' + q') + \frac{n_u'(n_e + n_i + q)}{\pi_s} \qquad (6)$$

$$I_{po} = \frac{n_u\, Q}{\pi_s \pi_t - n_u n_u'} \left(n_e' + \frac{n_u' n_e}{\pi_s} \right) = \frac{n_u\, Q}{\alpha} \cdot \frac{n_e' \pi_s + n_u' n_e}{(\pi_s)^2} \qquad (7)$$

(6) and (7) are the general expressions when the quencher acts both on S'-and T-states.

(6) and (7) are completely correct in the practical sense so long as the natural life of T-state is extraordinary long compared with that of S'-state which is $10^{-7}\sim10^{-8}$ sec.

When the quenching substance is absent, α and I_{po} in (6) and (7) are put as $\alpha^{(0)}$ and $I_{po}{}^{(0)}$ respectively, then the formulas for $\alpha^{(0)}$ and $I_p{}^{(0)}$ are given as follows.

$$\alpha^{(0)} = \pi_t{}^{(0)} - \frac{n_u n_e'}{\pi_s{}^{(0)}} = n_e' + n_i' + \frac{n_u'(n_e + n_i)}{\pi_s{}^{(0)}} \qquad (8)$$

$$I_{po}{}^{(0)} = \frac{Q}{\alpha^{(0)}} \cdot \frac{n_u(n_e' \pi_s{}^{(0)} + n_e n_u')}{(\pi_s{}^{(0)})^2} = \frac{Q}{\alpha^{(0)}} \cdot \frac{n_u\{n_e'(n_e + n_i + n_u) + n_e n_u'\}}{(n_e + n_i + n_u)^2} \qquad (9)$$

where

$$\pi_s{}^{(0)} = n_e + n_i + n_u$$
$$\pi_t{}^{(0)} = n_e' + n_i' + n_u'$$

Now when the quenching substance affects only T-state, a remarkably simple relation holds as described below. Putting α and I_{po} in this case as $\alpha^{(q')}$ and $I_{po}{}^{(q')}$, these are easily derived from (6) and (7). $\alpha^{(q')}$ and $I_p{}^{(q')}$ thus obtained, when compared with $\alpha^{(0)}$ and $I_p{}^{(0)}$ (eq. (8) and (9)), lead to the following relation.

$$\alpha^{(q')} = \alpha^{(0)} + q'$$

$$I_{po}{}^{(q')} = \frac{Q}{\alpha^{(q')}} \cdot \frac{n_u\{n_e' \pi_s{}^{(0)} + n_e n_u'\}}{(\pi_s{}^{(0)})^2} = \frac{Q}{\alpha^{(q')}} \cdot \frac{n_u\{n_e'(n_e + n_i + n_u) + n_e n_u'\}}{(n_e + n_i + n_u)^2} = I_{po}{}^{(0)} \frac{\alpha^{(0)}}{\alpha^{(q')}}$$

therefore

$$\frac{I_{po}{}^{(q')}}{I_{po}{}^{(0)}} = \frac{\alpha^{(0)}}{\alpha^{(q')}} \qquad (10)$$

Thus in this case, the inital intensity of phosphorescence and the average life is proportional to each other.

Next, when the quenching substance affects only S'-state, the result is not so simple as in the former case. The formulas for I_{po} and α in this case are as follows.

$$\alpha^{(q)} = n_s' + n_t' + \frac{n_u'(n_r + n_t + q)}{\pi_s} \qquad (11)$$

$$I_{po}{}^{(q)} \frac{Q}{\alpha^{(q)}} \quad \frac{n_u(n_s'\tau_s + n_r n_u')}{(\pi_s)^2} \qquad (12)$$

Comparing with (8) and (9)

$$\frac{I_{po}{}^{(q)}}{I_{po}{}^{(0)}} = \frac{\alpha^{(0)}}{\alpha^{(q)}} \times \frac{(n_r + n_t + n_u)^2}{(n_r + n_t + n_u + q)^2}$$

$$\times \frac{n_s'(n_r + n_t + n_u + q) + n_r n_u'}{n_s'(n_r + n_t + n_u) + n_r n_u'} \qquad (13)$$

From (13) it may be anticipated that the intensity of phosphorescence decreases remarkably in contrast to a rather small change of life; because on the right side of equation (13), the quenching factor (q) exists in the denominator as a quadratic term in addition to the ratio $\alpha^{(0)}/\alpha^{(q)}$. It may be mentioned that there exists (q) term in the numerator of the third factor, but at ordinary temperature, when the condition $n'_r \lesssim n'_u$ holds in many cases, the effect is presumably rather small.

To sum up the above results, one can hope to judge whether quenchers affect on S'-state or T-state predominantly, if one measures the initial intensity and average life of the quenched phosphorescence and compares them with those of unquenched one.

B. Apparatus and Procedure

The life of filter paper-Trypaflavine phosphor being of the order of 0.1 sec, it can be measured accurately by the use of electromagnetic oscillograph. But, the intensity being so weak that it is necessary to use a photomultiplier and amplify the photocurrent further to some extent. We have designed our apparatus to control the amplification in a wide range and at the same time, made use of a relay circuit to record, on the same oscillograph paper, the initial and the final stage of the one decay curve with the same order of accuracy. Two kinds of vessels were used for the sample; A) one is an ampule of a simple type, which contains a piece of filter paper (immersed previously in the aqueous solution of Trypaflavine and evacuated) close to the inner surface of the vessel. B) The other is of a Dewar-flask type with a ground joint, of which the vacuum part contains several kinds of samples fitted close arround the inner brass wall. The latter vessel is convenient for measuring at various temperatures. The details of the apparatus for the measurement and of the vessels of samples will be reported elesewhere.

C. Some of the Experimental Results

a) Results obtained with the vessel A. When the logarithm of the phosphorescence intensity is plotted against time, an almost straight line is obtained in most cases; some of the examples are shown in Fig. 2. It is

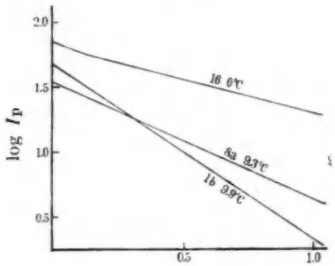


Fig. 2

certain that the decay curve is expressed by a single exponential form.

$$I_p = I_{po} e^{-\alpha t} \qquad (1)$$

where I_{po} is the initial intensity and α is the reciprocal of the average life or the decay constant.

From the inclination of the line one can easily calculate α, and by exterpolating the line to $t=0$ one can get the value I_{po} (relative). Some reults are tabulated in Table I.

TABLE I

α AND I_{po} AT VARIOUS DYE CONCENTRATION

Sample	Conc. of adsorbed dye 10^{-5} mol/g.	(at 10°C) α*	(Vessel A) I_{po} (relative)
1a		3.23	44
1b		3.07	31
„	15.3	3.13	47
„		3.05	49
2a		2.75	80
„	9.02	2.74	98
2b		2.62	75
3b		2.43	146
„	2.84	2.41	133
4		2.00	110
	1.11	2.00	123
		2.13	136
5	0.602	2.01	99
		1.98	68
6	0.361	1.94	75
7	0.241	2.08	50
8a		2.08	34
„	0.120	2.02	36
8c		2.04	34
8d		2.02	43
W1**	5.81	2.11	109
W2	1.11	1.92	141
W3	0.182	1.76	53

* The small temperature effect is corrected for the experimental value.

** The filter paper was washed with distilled water for a long time.

1. Reproducibility. As is seen from Table I, each measurement is quite reliable and the process of phosphorescence is quite reproducible so long as the treatment of the sample is the same, although a special pretreatment of the filter paper such as washing with distilled water for a long time gives a different α-value (cf. W in Table I).

2. Effect of Temperature. The result is that I_{po} scarcely depends upon the temperature, while α shows a conspicuous increase with the rise of temperature. The activation energy is calculated to be about several Kcal. by the use of Arrhenius equation. (Of course the calculation is approximate in nature and it was made merely for the purpose of correcting the experimental results in order to compare at the same temperature.

3. Effect of the Incident Light Intensity. Under the present experimental conditions, I_{po} is completely proportional to the intensity of incident light, while α does not depend upon it.

4. Effect of Concentration of Dye. When one plots the α-values and I_{po}-values against the dye concentration, curves as shown in Fig. 3 are obtained. In this figure a dotted curve is an adsorption isotherm plotted against the equilibrium concentration of the solution given along the right side ordinate.

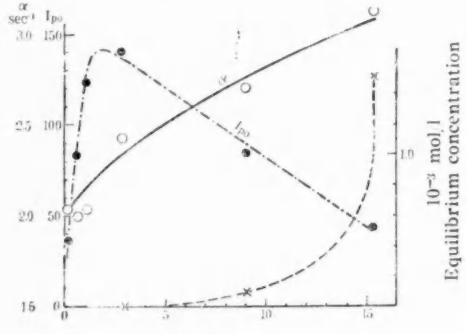


Fig. 3. I_{po} and α against the dye concentration (10°C) (Vessel A)

As is apparent from the figure, I_{po} increases quite rapidly in the range of small concentration, and after reaching a maximum, decreases almost linearly down to 1/3~1/4 of the maximum value in the region of saturated adsorption. On the contrary, α-value is almost constant in the region where I_{po} curve rises but thereafter it increases monotonously until it reaches the value about 30% larger than the original one.

b) The Results Obtained with the Vessel B. In this case log I_p~t curve shows a slight curvature at the initial stage and this curvature seems to increase with the concentration of dye (see Fig. 2). But the magnitude of this curvature being very small, α value was calculated from the linear part. The results at 0°C and 10°C are given in Table II and Fig. 4. I_{po} varies with the dye

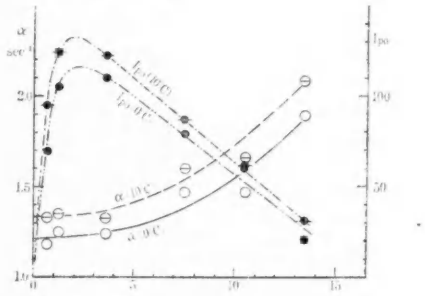


Fig. 4. I_{po} and α against the dye concentration (0°, 10°C) (Vessel B)

concentration in the same way as in the case of vessel A. α seems to show a different tendency from the former curve, the reason of which is not certain. But the magnitude of increase is quite the same as before.

TABLE II

α AND I_{po} AT VARIOUS DYE CONCENTRATION

(at 10°C and 0°C) (vessel B)

Sample	Conc. of adsorbed dye 10^{-6} mole/g	α 0°C	α 10°C	I_{po} 0°C	I_{po} 10°C
11	13.5	1.89	2.08	21	31
12	10.5	1.47	1.66	62	60
13	7.5	1.47	1.60	79	87
14	3.6	1.24	1.33	110	122
15	1.22	1.25	1.35	105	124
16	0.64	1.18	1.33	69	95

D. Discussion

It still remains open to question that the mechanism of organic phosphorescence, especially in the case of adsorbed phosphor, is completely explained by Lewis' model. But our results show quite definitely that the process is expressed as a unimolecular reaction and there is no reason to reject Lewis' scheme.

Let us consider, therefore, the concentra-

1) Filter paper used for this series was washed thoroughly with distilled water.

tion effect according to the results derived in (A) on the ground of Lewis' model. As seen from Fig. 3 and Fig. 4, $I_{po}\sim c$ and $\alpha\sim c$ curves show the same features for both cases at least qualitatively, and so the main characters of the phosphorescent process may be discussed upon the data of the present report, though the detailed discussion such as about the various transition probabilities may require more exact measurements.

In the present case, there is no special quencher added, but if the self-quenching due to the interaction of the adsorbed dye molecules exists, it may conventionally be represented by q and q'. Other transition constants n_s, n_t, n_u, n_s', n_t', n_u' might be affected by the dye concentration, but are approximated to be constant tentatively in the following discussion.

Let us consider at first how the rise of I_{po} in the low concentration region can be explained. In this region α is almost constant and therefore, the self-quenching can be neglected completely, and it may also be certain that all other transition probabilities keep the same value. Then, from (7) I_{po} must be proportional to Q, the number of molecules excited to S'-state per second during illumination (or the number of photons absorbed per sec.), which can be put as $(1-e^{-\varepsilon cd})$, where ε is the molecular extinction coefficient and cd is the number of moles of dye (in the ground state) in 1000 cm^2 of the cross section of the light path.

Now, as was stated in the previous section the intensity of phosphorescence is completely proportional to that of the incident light. Therefore, the state of affairs is far below the photosaturation and the number of molecules in the ground state can be put equal as an analytical quantity.

Now, it turned out that up to the region of max. I_{po}-value (about 1.11×10^{-5} mol/g), the experimental relation between I_{po} and c(analytical) could be expressed successfully by the equation

$$I_{po}=\text{const}\ (1-k^{-\varepsilon cd})$$

where ε is put as 7×10^4. With regard to the above value of ε, we could demonstrate that its order was very plausible by measuring the absorption coefficient for a cellophane Trypaflavine phosphor.

Thus it can safely be concluded that the increase of I_{po} in the region of small dye concentration is due to the increase of absorption of light.

Next, let us consider the high concentration region. Using the above ε value, it can be confirmed that beyond 2.2×10^{-5} mol/g. the absorption of light is more than 95% and so Q can be put as constant. Therefore, the decrease of I_{po} must be attributed to the selfquenching in the broad sense of the word.

The following three possible phenomena may be considered as the cause for the self quenching.

1) Accompanied with the increase of concentration, the dye molecules aggregate into such polymers (including dimers) that can not emit fluorescence nor phosphorescence at all.

2) The interaction between excited dye molecule and the neighbouring normal molecule causes the excess energy of the former to be dissipated into thermal energy.

In such a case, two possibilities must be discriminated.

a) The state affected is S'-state.

b) The state affected is T-state.

Of course it may be possible that the above three phenomena superpose. Among these three phenomena, the first is quite plausible in view of the fact that the absorption spectrum of Trypaflavine adsorbed on cellophane, changes conspiquously with the increase of dye concentration. Evidently, the electronic states in question (ground and excited states), in this case, are not concerned with a monomeric dye molecule but concerned, so to speak, a different molecular species. But there is no doubt that they are singlet states.

If 2b) is the case, then I_{po} must be reciprocally proportional to α, which contradicts the experimental results; thus I_{po} at 15×10^{-5} mol/g. of the dye concentration is only about one third of that at 1.5×10^{-5} mol/g., while the increase of α-value is about 30%.

Therefore the possibility that 2b) is the main and principal process of quenching is definitely denied. On the other hand 2a) does not contradict with the experimental results, since in this case I_{po} ought to decrease conspicuously in contrast to a rather small increase of α.

The conclusion is that the states related with the quenching process are chiefly singlet states, irrespective whether the mechanism be 1) or 2a).

Summary

Assuming Lewis' scheme, mathematical formulation was given for the decay of organic phosphorescence, which would help us to judge whether the quenching action of the added substance affects on singlet or triplet state. The decay curves of Trypa-

flavine-filter paper phosphor in various concentrations, were accurately measured by and oscillograph, and from the results obtained, it was tentatively concluded that the triplet state is not affected much in the concentration quenching.

Full accounts of the experiment and more detailed discussions will be published in Journ. Polytech. Osake City University.

The cost of this research has been partly defrayed from the Scientific Research Grant from the Ministry of Education, to which the present authors wish to express their gratitude.

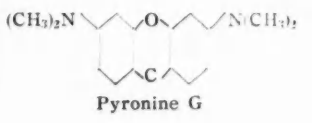
Institute of Polytechnics, Osaka City University, Osaka

Influence of the Addition of High Molecular Electrolytes upon the Absorption Spectra and Fluorescence of Organic Dyestuffs. II.

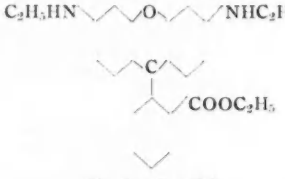
By Masao KOIZUMI and Noboru MATAGA

(Received August 19, 1953)

In the second paper[1] of our series of physicochemical studies of organic dyestuffs*,**, the influence or addition of K-polyvinylsulfate (PVSK) upon the absorption spectra and fluorescence of Rhodmaine 6G was reported, and the results were explained almost quantitatively as due to the change of aggregation of dye ions, which is caused by the accumulation of the latter in the neighbourhood of PVSK. Now in the course of our extensive study of the influence of PVSK upon various basic dyes, which was continued since then, we have found another interesting example which can be comprehended almost quantitatively as due to the change of aggregation of dye ions. It is Pyronine G, which



Pyronine G



Rhodamine 6G

belongs to Xanthen dyestuffs and its structure is somewhat more simple than Rhodamine 6G. In this case a new metachromatic band appears by the addition of PVSK, in contrast to the case of Rhodamine 6G, and yet the main features of the change of absorption spectrum are so simple and orderly that the quantitative treatment is possible. Pyronine G—PVSK system may be regarded as another ideal case of metachromasy which can be interpreted on the basis of the change of aggregation of dye ions.

Experimental

a) Some examples of the absorption spectra of Pyronine G in the aqueous solution at various concentrations are shown in Fig. 1.

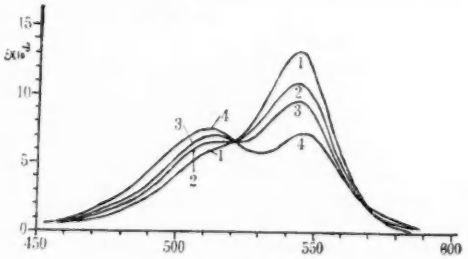


Fig. 1. Absorption spectra of the aqueous solution of Pyronine G.

	concentration	temperature
1.	5×10^{-5} mol/l	27°C
2.	2×10^{-4} „	
3.	6×10^{-4} „	
4.	2×10^{-3} „	

* Physicochemical Studies of Organic Dyestuffs in relation to Photochemistry. III.

** The paper will, hereafter, be refered to as Part I of "Influence of the addition of high molecular electrolytes upon the absorption spectra and fluorescence of organic dyestuffs".

1) M. Koizumi and N. Mataga, This Bulletin **26**, 165 (1953); See also: N. Mataga and M. Koizumi, *J. Inst. Polytech. Osaka City Univ.*, **S**, 21 (1952).

The absorption curve has two maxima at 545 mμ and 512.5 mμ. The former is prominent in the region of low concentration, while the latter gradually grows with the increase of concentration. Thus two maxima 545 and 512.5 mμ are expected to belong respectively to monomer (α-band) and dimer (β-band), an equilibrium existing between the two, as in the case of Rhodamine 6G[1,2,3,4]. (The equilibrium constant of dimerization was calculated to be 6.38×10^{-4} at 27°C.).

b) The effect of addition of PVSK is characteristic in its simplicity. Up to 2×10^{-4} mol./l. of dye the concentration, no change is produced in the spectrum. If the concentration of dye is a little above 4×10^{-4} mol./l. the absorption curve changes its shape with the addition of PVSK. Thus both α- and β-bands gradually decline apparently in a parallel way and a new metachromatic band appears at the position 800 Å shorter than the α-band, and it gradually grows with the addition of more PVSK. When the concentration of added PVSK reaches a certain critical concentration, however, the metachromatic band begins to decline accompanied with the rise of α- and β-band, until the shape of the curve coincides almost completely with that of the aqueous solution without PVSK. But as the concentration of dye increases, the phenomenon of recovery commences at a larger concentration of PVSK, and at last, when the dye concentration is about 2×10^{-3} mol./l. the recovery occurs only very slightly. (See Fig. 2)

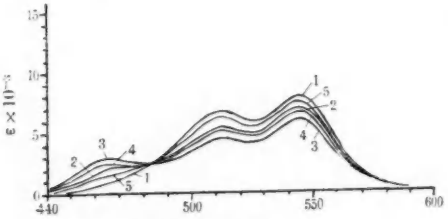


Fig. 2. Change of absorption spectra of Pyronine G by the addition of PVSK. (Dye conc. 8×10^{-4} mol./l.)

	PVSK	temperature
1.	0 and 1000 (7.56×10^{-5}gr/cc)	27°C
2.	5	,,
3.	10	,,
4.	50	,,
5.	500	,,

If one compares the above result with that of Rhodamine 6G[1], the chief points of difference are the rise and fall of α- and β-band occuring apparently in a parallel way, and the appearance of a new metachromatic band. As regards to the phenomenon of recovery, it is qualitatively similar to that in the case of Rhodamine 6G, but it is more elegant and complete in the region of low concentration of dye. It may be worthy to add that the positions of α-, β- and metachromatic band are invariable during the whole change.

Discussion

Let us consider the mechanism of metachromasy in the present case on the ground of the following experimental results.

1) Below 2×10^{-4} mol./l. of the dye concentration, no change is produced in the absorption spectrum, even if large excess of PVSK is added.

2) In the case of dye concentration a little above 4×10^{-4} mol./l. the addition of PVSK produces a metachromatic band with the fall of α- and β-band, but with the excess of added PVSK the spectra become similar to that of pure aqueous solution.

3) When the concentration of dye is increased furthermore, the change of absorption spectra, including the appearance of a metachromatic band, becomes more prominent and at the same time, the recovery is retarded and quite reduced.

To explain the result (1), we must recognize one of the following two situations.

A) The change of the electronic state of dye ions may be produced by their interaction with the electrolyte ions, but in the region of low concentration of dye, the number of interacted molecules, is so small that it cannot be observed as any change in spectra (It may alternatively be said that there is approximately no adsorption, provided that the model of adsorption[1] is adopted.)

B) Dye ions are adsorbed on the high molecular substance, but neither the equilibrium between monomer and dimer, nor the optical properties of both monomer and dimer in relation to the absorption spectrum, are affected by the adsorption.

Of the two possibilities mentioned above, A) cannot be reconciled with the facts (2) and (3) consistently. Thus the fact (3) might be attributed to the increase of adsorption (though small), but as long as one recognizes A), the quantity of adsorbed dye is so small as compared with the added high molecular substance, that the conditions around the adsorbed dye ion cannot be expected to be affected much by the addition of excess PVSK. Therefore, the fact (2) cannot be explained along this line, and some additional assumption is necessary. For example, if the structure of high molecular substance changes, in the region of its high concentra-

2) V. L. Levshin, *Acta Physicochim. U. R. S. S.* **1**, 684 (1935).

3) E. Rabinowitch and L. F. Epstein, *J. Am. Chem. Soc.*, **63**, 69 (1941).

4) S. E. Sheppard, *Rev. Mod. Phys.*, **14**, 303 (1942); S. E. Sheppard and A. L. Geddes, *J. Am. Chem. Soc.*, **66**, 1995, 2003 (1944).

tion, so remarkably in such a manner that it cannot adsorb the dye ions any longer, then the fact (2) could be explained. But this is also improbable in view of the fact (3) and also of the equilibrium dialysis experiment of Levine and Schubert[5].

The conclusion is, therefore, that one must assume the situation B). According to B), the fact 3) can be interpreted, for example, as due to the formation of a multiple associate of dye ions in the region of high concentration of dyes, and the result 2) can naturally be expected since the concentration of adsorbed dye ions decreases with the addition of an excess quantity of PVSK.

On the ground of the above qualitative deduction, it is much probable to attribute the change of absorption spectra of Pyronine-G, induced by the addition of PVSK, to a change of aggregation of dye ions.

Let us criticize this idea more quantitatively in the region of small concentration of dye, where the quantitative treatment is possible. Assume that in a certain range of the concentration of adsorbed dye ions, there is formed a new molecular species other than normal monomer and dimer, which produces a metachromatic band and it does not participate in monomer-dimer association equilibrium. (It may be added that this molecular species is probably a multiple associate but the calculation below does not necessarily require to be so).

Molar extinction coefficients at the position of α- and β-maximum in the pure aqueous solution are correlated with the experimentally obtained extinction coefficient λ by the following equations.

$$\left.\begin{aligned}\lambda_m &= C_0\varepsilon_m \\ \lambda_d &= C_0\varepsilon_d\end{aligned}\right\} \qquad (1)$$

where C_0 is the analytical concentration of dye (mol./l.) and ε_m, ε_d are the molar extinction coefficients at α- and β-maxima, respectively.

Now, when PVSK is added enough for a new molecular species to appear, the concentration of dye ions participating in association equilibrium may be reduced to some extent. If the reduced concentration be put as $(C_0-\Delta C_0)$, then the molecular extinction coefficient ε_m', ε_d' at the present condition ought to be given as follows:

$$\left.\begin{aligned}\lambda_m' &= C_0\varepsilon_m' = (C_0-\Delta C_0)\varepsilon_m \\ \lambda_d' &= C_0\varepsilon_d' = (C_0-\Delta C_0)\varepsilon_d\end{aligned}\right\} \qquad (2)$$

It is to be added that the above relations (2) assume that a pure metachromatic band is negligible at the position of α- and β-maximum, which is very much plausible in view of the experimental results.

From (2), the following relations must hold.

$$\varepsilon_m' = \frac{(C_0-\Delta C_0)}{C_0}\varepsilon_m,\quad \varepsilon_d' = \frac{(C_0-\Delta C_0)}{C_0}\varepsilon_d \qquad (3)$$

$$\frac{\varepsilon_m'}{\varepsilon_d'} = \frac{\varepsilon_m}{\varepsilon_d}$$

Thus if one calculates and tabulates previously, $\frac{\varepsilon_m}{\varepsilon_d}$-values against various concentrations of dye from the spectrum of the pure aqueous solution, then by comparing the experimentally obtained $\frac{\varepsilon_m'}{\varepsilon_d'}$-value with the table, one can decide the value of $(C_0-\Delta C_0)$ or ΔC_0.

The value of $\frac{(C_0-\Delta C_0)}{C_0}\varepsilon_m$, obtained by the above procedure ought to coincide with ε_m' as long as the starting assumption is correct. The results of the calculation satisfy this requirement almost completely as shown in Table 1.

TABLE I

COMPARISON BETWEEN ε_m' AND $\frac{(C_0-\Delta C_0)}{C_0}\varepsilon_m$

a) Concentration of dye $C_0=8\times10^{-4}$ mol./l.

P*	0	1	5	10	50	100	500	1000
$\Delta C_0(\times10^4)$	0	0.1	1.6	2.0	1.4	1.4	0.1	0
ε_m'	8.0	7.95	7.0	6.1	6.7	7.1	7.6	7.8
ε_m	8.0	8.2	8.8	9.0	8.7	8.7	8.2	8.0
$\frac{(C_0-\Delta C_0)}{C_0}\frac{\varepsilon_m}{\varepsilon_m'}$	1.0	1.0	1.0	1.1	1.0	1.0	1.0	1.0

5) A. Levine and M. Schubert, *J. Am. Chem. Soc.*, **74**, 5702 (1952).

b) Concentration of dye $C=10^{-5}$ mol./l.

P	0	1	5	10	50	100	500	1000
$\Delta C_0(\times 10^4)$	0	1.4	2.4	3.4	3.8	3.9		1.8
ε_m'	7.7	8.2	6.75	5.7	4.5	4.9		6.3
ε_m	7.7	8.0	8.7	8.8	8.9	8.94		8.0
$\frac{(C_0-\Delta C_0)}{C_0}\frac{\varepsilon_m}{\varepsilon_m'}$	1.0	0.8	0.97	1.0	1.2	1.1		1.0

* P: Quantity of PVSK added (Unit.: 7.56×10^{-5} g./cc.)

Thus it has been quantitatively proved that what produces a metachromatic band behaves as a new molecular species and lies outside monomer-dimer equilibrium. There scarcely remains any doubt that this new molecular species is polyassociate and is neither monomer nor dimer attached to PSVK in views of the qualitative discussion already stated. It is possible to discuss quantitatively other possibilities than the above one which is most probable, but the detailed discussion including them will be reported in Journ. Polytech. Osaka City University, with the full account of experimental results.

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Influence of the Addition of High Molecular Electrolyte upon the Absorption Spectra and Fluorescence of Organic Dyestuffs. III.

By Noboru MATAGA and Masao KOIZUMI

(Received August 19, 1953)

Introduction

In the first paper[1] of the series of investigation about "the influence of the addition of high molecular electrolyte upon the adsorption spectrum and intensity of fluorescence of dyestuffs", it was stated at first that two kinds of mechanisms for metachromasy are to be taken into account in order to treat the problem from a general standpoint.

One is a) the change of electronic state of dye ions, directly produced by their interaction with high molecular electrolyte, and the other is b) the change in the state of aggregation of dye ions, which is caused by the accumulation of dye ions in the neighbourhood of high molecular electrolyte. In that paper, we succeeded in interpreting quantitatively the behaviour of Rhodmaine 6G–PVSK system, in which no metachromatic band appears, upon the basis of monomer-dimer equilibrium. In Part II we gave strong evidence that the spectral behaviour of Pyronine G–PVSK system, in which a metachromatic band appears, can also be explained only by the change of aggregation of dye.

Hitherto we have intentionally chosen such systems in which the change of aggregation is expected to be important, and the above two examples are the ideal case of b) which are interpreted quantitatively. Among various dyes so far investigated, there are many which can be comprehended along the same line, though not so quantitatively and accordingly not so definitely as the above two examples.

Now, turning our attention to the other case, we have chosen various Na and K-alkyl sulfate esters of different chain length as the electrolyte with only one functional group, and studied their influences upon the absorption spectra and fluorescence intensities of many dyes, in order to find out such a system as can be interpreted as an ideal case a).

As a result of a systematic study of many dyes, it has been confirmed quite definitely that in such cases the change of aggregation of dye ions still plays an important role. In addition, we have obtained some evidences which suggest that prior to micell-formation (at which a remarkable change of absorption spectrum and fluorescence intensity occurs,

* Physicochemical Studies of Organic Dyestuffs in relation to Photochemistry IV.

1) M. Koizumi and N. Mataga, This Bulletin **26**, 115 (1953), See also: N. Mataga and M. Koizumi, *J. Inst. Polytech. Osaka City Univ.*, **3**, 21 (1952).

as is observed usually in other cases[2]) the high molecular electolyte lies in some aggregated state or in an orderly array of some kind. By virtue of it, the dye ions also take such a special state of aggregation as produce a peculiar type of change in absorption spectra and intensity of fluorescence.

In this paper some experimental results which support the above viewpoint, especially those about Rhodamine 6G, will be reported in a rather condensed form, the details of which will be published in Journ. Inst. Polytech. Osaka City University.

The chief points which we have investigated are 1) the effect of chain length of alkyl sulfate, 2) the effect of the dye concentration and 3) the effect of temperature.

The discussion will be given not separately but along with the experimental results in each part.

Experimental Results and Interpretation of Them

(1) The Effect of Chain Length of Alcohol Sulfate Ester—Methyl and butyl sulfate do not affect the spectrum nor the fluorescence at all, irrespective of the magnitude of addition. Amyl sulfate gives a slight effect only at its high concentrations. In the case of octyl sulfate, the quenching of fluorescence is observed accompanied by the complicated change of absorption in the region above 5×10^{-4} mol./l. When the concentration reaches C. M. C., the fluorescence recovers and the spectrum becomes simple again similar to that of pure aqueous solution.

Na-lauryl sulfate (LASNa) shows an analogous effect as octyl sulfate except that the effect becomes observable at a little lower concentration, ca. 10^{-5} mol./l. Analogous phenomena are also observed in some dyestuffs other than Rhodamine 6G such as Trypaflavine and Acrydine yellow, which have a tendency to polymerize in the pure aqueous solutions [1,3]) while Rhodamine B, which does not dimerize in the aqueous solution[1]) suffers no effect, however much LASNa is added. All these results strongly support the view that only in the case when such electrolytes as can form the micelle are added to dimerizable dyestuffs, the fluorescence is quenched and the absorption changes prior to C. M. C.

(2) The Effect of the Concentration of the Dye.—When the dye concentration is small (2×10^{-6} mol./l.), the effect comes to be observed at higher concentration of LASNa while the recovery of fluorescence begins at a far lower concentration than C. M. C. reported in the literatures[4]), which was determined, for example, from the measurement of electric conductivity. As regards the absorption spectrum, α-band declines and β-band slightly rises in the region where the quenching of fluorescence is remarkable. The above results can be comprehended if the dye ions in the proper concentration of added LASNa are assumed to exist as something like dimer sandwiched in between the ions of added electrolytes, and have no power of fluorescence. The interpretation is quite analogous to the case of PVSK. Thus when the concentration of dye is low, the gradual increase of LASNa soon comes to provide, prior to C. M. C., such a situation in which the dye ions in the neighbourhood of the aggregate of LASNa begins to decrease, and this causes the above phenomenon of recovery.

On the other hand, when the concentration of dye is large, the quenching is observed in a wider range of concentration of LASNa, and the magnitude of quenching is more remarkable than in the case of lower concentration of dye. Quenching is removed sharply in the close neighbourhood of C. M. C. of LASNa. As for the absorption spectra, both α-and β-band decline at first, with the addition of LASNa ; then a broad band appears extending to the longer wave length than α-maximum, which in the suitable concentration of LASNa has two peaks in the opposite side of the position of α-band. Thus the spectrum is quite different from that of simple or PVSK added[1]) aqueous solution, and this result may reasonably be comprehended if one assumes that dye ions are sandwiched in between the orderly array of electrolyte, and interaction between these dye ions are such that the situation is somewhat analogous to but different from that of dimerization or polymerization in the aqueous solution. It goes without saying that the quenching is also interpreted on the basis of the same model. It may be added that in the case of high concentration of dye, the number of sandwiched dye ions between the orderly array of electrolyte ions would be so large that it could not be decreased so much, prior to C. M. C., and this may be the reason why the recovery takes place at C. M. C. without any sign of it beforehand. The similar changes in absorption spectrum and intensity of fluorescence are also observed in the case of other dyes which

2) See for example; M. L. Corrins and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 683 (1947); *J. Chem. Phys.*, **14** 641 (1946), R. C. Merriil and R. Getty, *J. Phys. Colloid Chem.*, **52**, 774 (1948).

3) V. Zanker, *Z. Phys. Chem.*, **199**, 225 (1952).

4) See for example; F. D. Haffner, G. A. Piccione and C. Rosenblum, *J. Phys. Chem.*, **46**, 662 (1942).

have some tendency of polymerization such as Trypaflavine and Acridine yellow[1,3] and they are also considered to be due to the same circumstances. On the other hand, Pyronine G which sustains no effect by PVSK in the small concentration of dye (Part II), also shows no change in either absorption spectrum or fluorescence in the present case, as long as the concentration of dye is low. As for Rhodamine B which has no tendency of polymerization, the result was already mentioned in section 1.

The difference of spectrum in the case of LASNa from that with PVSK seems to exist generally. Thus Pyronine G, in a very limited region of dye concentration, shows a similar metachromatic band as in the case of PVSK, but elswhere, it commonly gives a broad band different from that of the aqueous solution. Other dyestuffs such as Thionine and Toluidine blue etc., show similar behaviour. The problem would be worthy of further study with regards to the change of electronic state of dye ion influenced by the ions of electrolyte.

Judging from the above results, it may be safe to conclude that the change of spectrum and fluorescence in the case of LASNa is essentially related to the change in aggregation of dye ions just as in the case of PVSK.

(3) The Effect of Temperature.—The intensities of fluorescence were measured at 13° C. and at 55°C. in various corresponding conditions and were compared with each other. It was found that as long as the concentration of dye is small (2×10^{-6} mol./l.), the intensity is reduced by the elevation of temperature when the quantity of added LASNa is small (up to 2×10^{-4} mol./l.); while at higher concentration of LASNa the intensity is stronger at a higher temperature. Now, as for the effect of temperature, two phenomena must in general be taken into account. One is the collisional quenching[5], which increases at higher temperature, and the other is the shift of association equilibrium between dye ions or between electrolyte and dye ion, which generally tends toward dissociation at higher temperature. If it is assumed that the above two effects are operative in the present system, then the results can at least qualitatively be well interpreted. Thus the collisional quenching naturally predominates at low concentration of LASNa where the aggregates of LASNa are not existent in measurable quantity, and the result is that the intensity is reduced at higher temperature. While at higher concentration of LASNa, a relatively large portion of dye ions are sandwhiched in between the orderly array of LASNa ions, and the shift of association equilibrium determines the resultant temperature effect. According to the above interpretation, the temperature effect ought to be, in general, positive at higher concentration of dye, and the experimental result is just as expected.

It may further be added that the features of absorption spectrum becomes relatively simpler at higher temperature, which is also reconciled with the above interpretation. Thus the temperature effect can also be comprehended if one assumes that the dye ions sandwiched in between the orderly array of electrolyte ions, interact with each other in a somewhat similar manner as in the bulk solution.

General Conclusion

From the above-mentioned experimental results and discussions, it has become quite clear that the change of absorption spectra brought about by the addition of an electrolyte with only one functional group, is essentially correlated with the change of aggregation of dye ions. But, in contrast to such substances with many functional groups as PVSK, it seems indispensable that some kind of specific aggregation or orderly array of ions exists on the part of added electrolyte. The structure of it is naturally considered to be quite labile, and accordingly the aggregation of dye ions, an orderly array of electrolyte ions and the interaction between dye and electrolyte ions, all these phenomena, are entangled with each other in so delicate a manner that the spectrum is expected to be influenced by various factors very sensitively as is the case.

This problem would be very interesting from the standpoint of the change of electronic state of dye affected by the neighbouring electrolyte ion, that is from the standpoint of case (a) mentioned at the beginning of the present paper.

To sum up our results reported in three papers, it can be concluded that in the case of basic dyes such as Xanthene or Thiazine dyestuffs, metachromasy produced by the addition of anionic electrolyte is chiefly caused by the change of aggregation of dye ions (mechanism b) though the change of electronic state of dye directly produced by the interaction between dye and electrolyte ions (mechanism a) may be superposed in some cases. Our general conclusion is quite similar to that of Michaelis[6], but our reasoning is more

5) See for example: P. Pringsheim, "Fluorescence and Phosphorescence", 322. 349 (1949).

6) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **67**, 1212 (1945), L. Michaelis, *J. Phys. Colloid Chem.*, **54**, 1 (1950).

definite being supported by some quantitative discussions.

More detailed discussions involving other dyestuffs will be reported in Journ. Inst. Polytech. Osaka City University. The cost of this reseach has been partly defrayed from the Scientific Grant from the Ministry of Education.

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Hydroxylamine dans les eaux lacustres[1]
—Variation saisonnière et importance biogéochimique—

Par Motoharu TANAKA

(Reçu le 23 Décembre 1953)

Les recherches nombreuses[2] sur les azotes combinés dans l'hydrosphère ne datent pas d'aujourd'hui. D'un autre côté, les biochimistes et les bactériologistes étudient sans cesse les mutuelles transformations bactériologiques des azotes combinés.

Récemment, les biochimistes ont démontré la production intermédiaire d'hydroxylamine dans le cas de transformation $NO_2^- \rightleftarrows NH_3$. Ainsi Novak et Wilson[3] ont constaté la formation d'hydroxylamine au cours de la fixation d'azote, et Taniguchi et d'autres[4] l'ont verifiée dans la réduction successive de l'azote nitrique. Procédant par méthode indirecte, Lees[5] a conclu la possibilité d'une formation intermédiaire d'hydroxylamine dans la nitrification bactériologique.

Nous avons déjà présenté une étude[7] sur l'existence d'hydroxylamine dans les eaux lacustres. Dans le présent exposé nous allons compléter les résultats d'observation durant une année entière. L'argumantation en sera faite dans le détail.

Lac étudié Pour cette recherche nous avons choisi le lac Kizaki. La stratification très prononcée des azotes combinés y est observée dans la période de stagnation estivale[7].

Le lac Kizaki se trouve dans la Préfecture de Nagano, le long de la vallée, au pied Est des Alpes Japonaises Nord. Par une rivière il se trouve mis en communication avec le lac Nakatsuna. Sa transparence de quelques mètres nous montre sa nature mésotrophiqe.

Méthode d'analyse Nous avons employé la modification par Endre et Kaufmann[8] de la méthode de Blom[9], dans laquelle l'hydroxylamine est oxydée en nitrite avec une solution d'iode; avec l'acide sulfanilique le nitrite forme un composé diazoïque qui est subséquemment couplé avec l'α-naphtylamine en produisant une coloration rose. On compare cette coloration et en déduit la teneur en hydroxylamine.

Les réactifs nécessaires sont:

Acide sulfanilique Mélanger 10.5 g. d'acide sulfanilique, 6.8g. d'acétate de sodium, 300cc. d'acide acétique cristallisable et 600 cc. d'eau distillée. Faire bouillir la solution et diluer à 1 litre.

α-Naphtylamine A un litre d'eau distillée, bouillante, ajouter 5.0 g. d'α-naphtylamine et continuer l'ébullition pendant 5 minutes. Filtrer immédiatement et introduire l'acide chlorhydrique suffisant pour clarifier la solution.

Iode 1.3 g. d'iode est dissous dans 100 cc. d'acide acétique cristallisable.

Hyposulfite 2.5 g. d'hyposulfite de sodium sont dissous dans 100 cc. d'eau distillée. Conserver en glacière. Tous les réactifs doivent être contenus dans des bouteilles brunes.

Mode opértoire de l'analyse A 5 cc. d'échantillon d'eau, ajouter 1 cc. d'acide sulfanilique et 0.5 cc. d'iode: maintenir la température de la solution à 30–40°C pendant 15 minutes; décolorer ensuite l'excèsd'iode avec l'hyposulfite. Y introduire 1 cc. d'α-naphtylamine et comparer la coloration avec celle qu'on obtient par le nitrite de sodium, parce que l'oxydation de l'hydroxylamine en nitrite est vraiment quantitative.

S'il existe du nitrite dans l'échantillon, soustraire son équivalence de la teneur obtenue en hydroxylamine.

Résultats d'observations Nos observations ont débuté au mois de juin 1952 et ont été poursuivies jusqu'en mars 1953 par intervalle

1) Cet exposé a été déjà présenté à l'assemblée annuelle de la société chimique de Japon qui s'est tenue à Kyoto au mois d'avril 1953.

2) Par example, B. P. Domogalla, E. B. Fred et W. H. Peterson, *J. Amer. Water Works Assoc.*, **15**, 369 (1929); S. Yoshimura, *Archiv f. Hydrobiol.*, **24**, 155 (1932).

3) R. Novak et P. W. Wilson, *J. Bact.*, **55**, 517 (1948).

4) S. Taniguchi, H. Mitsui, J. Toyoda, T. Yamada et F. Egami, *J. Biochem.*, **40**, 1775 (1953).

5) H. Lees, *Nature*, **169**, 156 (1952).

6) M. Tanaka, *Nature*, **171**, 1160 (1953).

7) M. Tanaka, *J. Earth Sciences, Nagoya University*, **1**, 119 (1953).

8) G. Endres et L. Kaufmann, *Ann. Chem.*, **53**, 184 (1937).

9) J. Blom, *Biochem. Z.*, **194**, 385 (1928).

de trois mois. Les tableaux 1–4 nous montrent les rèsultats.

En juin, l'eau de lac se stratifie, et on constate vers le fond que l'oxygène tend légèrement à diminuer. Le nitrite et l'hydroxylamine ne sont décelés qu'à la couche de 15 m., c'est-à-dire au-dessous de la "couche du saut". Quant au nitrate, il se trouve dans les couches au-dessous de 17.5 m. et il augmente avec la profondeur. La teneur en azote ammoniacal oscille entre 0.012 et 0.030 mg. par litre.

Au mois de septembre, la stagnation se complète et les eaux au-dessous de 25 m. contiennent moins d'un cc. d'oxygène par litre d'eau. On décèle du fer ferreux dans la couche tout près du fond. L'azote nitrique augmente jusqu'à la couche de 26 m. et il diminue au

TABLEAU I

DISTRIBUTION VERTICALE DE L'OXYGÈNE ET DES AZOTES COMBINÉS DANS LE LAC KIZAKI (a)

Le 3 juin 1952* Profondeur atteinte: 29 m.

Profondeur m	Température °C	O_2 cc/l	$N\text{-}NO_3$ mg/l	$N\text{-}NO_2$ mg/l	$N\text{-}NH_2OH$ mg/l	$N\text{-}NH_3$ mg/l
0	16.25	6.69	<0.02	<0.001	<0.001	0.018
2.5	15.78	7.07	"	"	"	0.012
5	15.68	6.83	"	"	"	0.016
7.5	13.71	6.83	"	"	"	0.030
10	9.93	7.04	"	"	"	0.016
12.5	8.83	6.84	"	"	"	<0.01
15	8.08	6.02	"	0.0075	tr.	"
17.5	7.36	6.02	0.04	<0.001	<0.001	0.012
20	6.81	6.03	0.04	"	"	<0.01
22.5	6.60	5.99	0.06	"	"	0.018
25	6.42	5.88	0.05	"	"	0.018
27.5	6.40	5.22	5.22	"	"	0.018
28.8	——	4.63	0.06	"	"	0.018
28.9	——	4.63	0.06	"	"	0.022
28.95	——	4.79	0.07	"	"	0.030
29.0	——	5.07	0.04	"	"	0.030

* Dans toutes les couches d'eau, on ne décèle aucune trace de fer ferreux.

TABLEAU II

DISTRIBUTION VERTICALE DE L'OXYGÈNE ET DES AZOTES COMBINÉS DANS LE LAC KIZAKI (b)

Le 5 sept. 1952 Profondeur atteinte: 28.5 m.

Profondeur m	Température °C	O_2 cc/l	$N\text{-}NO_3$ mg/l	$N\text{-}NO_2$ mg/l	$N\text{-}NH_2OH$ mg/l	$N\text{-}NH_3$ mg/l
0	24.8	5.77	<0.02	<0.001	<0.001	<0.01
2.5	24.71	5.67	"	"	"	0.018
5	24.60	5.43	"	"	"	0.018
7.5	18.90	5.71	"	"	"	0.018
10	13.82	4.86	"	"	"	0.016
12.5	10.76	4.33	0.08	"	"	0.016
15	9.74	4.30	0.07	"	"	0.018
17.5	——	4.08	0.15	"	"	0.018
20	——	1.98	0.20	"	"	0.016
22.5	——	1.73	0.16	"	"	0.018
25	——	0.56	0.28	"	"	0.018
26	——	——	0.28	0.004	0.004	0.018
27.5	——	——	0.19	0.012	0.007	0.016
28	——	——	0.11	0.014	0.011	0.016
28.1	——	0.42	0.09	0.016	0.011	0.020
28.3	——	0.31	0.08	0.019	0.011	0.020
28.45	——	0.49	0.06	0.019	0.011	0.020
28.50*	6.60	0.53	0.05	0.015	0.021	0.023

* Apparition de fer ferreux.

TABLEAU III

DISTRIBUTION VERTICALE DE L'OXYGÈNE ET DES AZOTES COMBINÉS DANS LE LAC KIZAKI (c)

Le 8 déc. 1952 Profondeur atteinte: 28.7 m.

Profondeur m	Température °C	0_2 cc/l	$N\text{-}NO_3$ mg/l	$N\text{-}NO_2$ mg/l	$N\text{-}NH_2OH$ mg/l	$N\text{-}NH_3$ mg/l
0	8.5	6.52	<0.02	<0.001	<0.001	<0.01
5	8.63	6.47	0.09	〃	〃	〃
10	8.25	6.55	0.03	〃	〃	〃
15	8.65	5.90	0.04	〃	〃	〃
20	8.60	0.71	0.02	〃	〃	0.016
21.5	—	—	0.025	0.006	0.004	<0.01
22.5*	8.42	0.82	<0.02	0.005	0.005	0.025
24	—	—	〃	<0.001	tr.	0.030
25	8.52	0.74	〃	〃	<0.001	0.032
25.5	—	—	〃	〃	〃	0.032
26.5	—	—	〃	〃	〃	0.035
27.5	8.65	1.51	〃	〃	〃	0.035
28.3	—	—	〃	〃	〃	0.040
28.5	—	0.71	〃	〃	〃	0.040
28.6	—	—	〃	〃	〃	0.040
28.65	—	0.61	〃	〃	〃	0.045
28.7	7.02	0.71	〃	〃	〃	0.045

* Au-dessous de cette couche existence de fer ferreux.

TABLEAU IV

DISTRIBUTION VERTICALE DE L'OXYGÈNE ET DES AZOTES COMBINÉS DANS LE LAC KIZAKI (d)

Le 2 mar. 1953* Profondeur atteinte: 26.5 m.

Profondeur m	Température °C	0_2 cc/l	$N\text{-}NO_3$ mg/l	$N\text{-}NO_2$ mg/l	$N\text{-}NH_2OH$ mg/l	$N\text{-}NH_3$ mg/l
0	3.3	8.55	<0.02	<0.001	<0.001	0.014
5	3.04	8.35	0.02	〃	〃	0.022
10	3.10	8.22	<0.02	〃	〃	0.022
15	3.10	8.38	〃	〃	〃	0.022
20	3.10	8.99	〃	〃	〃	0.022
25	—	8.52	〃	〃	〃	0.022
26.3	—	8.18	〃	〃	〃	0.025
26.45	—	8.35	〃	〃	〃	0.022
26.5	3.05	7.72	0.06	〃	〃	0.022

* Aucune trace de fer ferreux dans les couches d'eau.

delà de cette couche.

C'est dans cette couche que l'hydroxylamine et le nitrite apparaissent en proportion du décroissement de l'azote nitrique. Le nitrite atteint son maximum entre 20 et 5 cm. au-dessus de la superficie de la vase. La teneur en hydroxylamine est la plus forte dans la couche la plus basse (la couche tout près du fond). L'ammoniaque varie de 0.016 à 0.023 mg. par litre.

A la fin de la période de stagnation, en décembre, on décèle du fer ferreux au-dessous de 22.5 m., bien que la stabilité verticale ne soit pas assez grande. On peut doser l'azote nitrique entre les profondeurs 5 et 21.5 m m.; sa teneur varie de 0.02 mg. jusqu'à 0.09 mg. par litre. L'hydroxylamine et le nitrite sont décelables aux couches de 21.5 m. et de 22.5 m. La teneur en hydroxylamine est supérieure dans cette dernière couche où le nitrite est moins abondant. L'ammoniaque apparaît dans les couches au-dessous de 20 m. et ses concentrations y sont de 0.016 à 0.045 mg. par litre.

Après la circulation hivernale, en mars 1953, on ne décèle le nitrate qu'à la profondeur de 5 m. et tout près du fond. On ne constate plus l'existence d'hydroxylamine et de nitrite dans aucune couche d'eau. Les teneurs en azote ammonical oscillent entre 0.014 et 0.026 mg. par litre.

Résumons nos résultats—A mesure que la période de stagnation avance, l'hydroxyl-

amine apparaît dans les couches dont la teneur en oxygéne est inférieure à 1 cc par litre d'eau.

Le maximum est atteint à la partie la plus haute des couches où l'on décèle le fer ferreux (niveau d'oxydo-réduction). Au-dessous, l'hydroxylamine diminue et disparaît. A ce dernier point de vue il ressemble au nitrite, mais leurs tenenrs les plus fortes apparaissent aux couches différentes; vers le fond, dans la période de stagnation, on observe comme suit les maxima des teneurs en azotes combinés: nitrate, nitrite, hydroxylamine et ammoniaque.

Après la circulation hivernale, on ne décèle ni nitrite ni hydroxylamine dans aucune couche d'eau.

Argumentation Considérons d'abord comment se forme l'hydroxylamine dans les eaux du lac Kizaki:

Avant l'apparition d'hydroxylamine, le nitrate est le plus abondant parmi les azotes combinés (Tableau I). L'augmentation de l'hydroxylamine et du nitrite correspond à la diminution du nitrate et de l'oxygène (Tableaux II et III).

En nous appuyant sur ces deux faits, nous pouvons conclure que l'hydroxylamine dans ce lac se forme comme produit intermédiaire de la réduction bactériologique du nitrate favorisée par l'environment pauvre en oxygène.

L'apparition du nitrite (et probablement de l'hydroxylamine) à la profondeur de 15 m. en juin 1952 (Tableau I) est plus dfficile à expliquer, car on n'y constate pas la diminution d'oxygène. Cette profondeur correspond à "compensation depth" où l'assimilation et la décomposition des matières organiques sont presque égales. Bien que l'on y puisse supposer un milieu microscopiquement anaérobie où des bactéries peuvent réduire le nitrate en nitrite, ce phénomène serait plus probablement dû à la réduction du nitrate par les êtres autotrophes, par exemple algues, au fur et à mesure de l'assimilation de l'azote nitrique dans l'épilimion. On sait que l'algue peut réduire le nitrate dans un milieu aérobie, comme récemment Kessler[10] l'a étudié en détail à l'aide de la méthode biochimique. On peut ainsi expliquer de plus la présence de nitrate au-dessous de 15 m. et son absence au-dessus de cette couche.

Résumé

1° Nous avons étudié la variation saisonnière des composés d'azote, surtout celle de l'hydroxylamine.

2° Dans le lac Kizaki, à la période de stagnation, nous avons trouvé de l'hydroxylamine au niveau d'oxydo-réduction.

3° Nous avons conclu que cet hydroxylamine est un produit intermédiaire de la réduction bactériologique du nitrate.

4° L'apparition de l'azote nitreux (et probablement de l'hydroxylamine) au-dessous de la "couche du saut", au début de la période de stagnation, serait due sans doute à la réduction de l'azote nitrique par les algues.

En terminant ce compte-rendu, nous tenons à mentionner les noms des MM. les Professeurs K. Sugawara et F. Egami à qui va notre gratitude pour l'aide précieuse qu'ils n'ont pas cessé de nous donner.

Institut de chimie, Faculté des Sciences, Université de Nagoya

10) E. Kessler, *Flora*, **140**, 1 (1953).

Rheology of Surface Films. II. A Surface Rheometer for Measuring the Film Creep under Constant Shear Stress[1]

By Kiyoshi INOKUCHI

(Received February 18, 1954)

Introduction

In a previous paper[2], it has been proved that the rheological study of monomolecular films is a valuable tool for gaining more insight into the structure of materials. Before further development of this study is attempted, it is first necessary to establish the standard procedure of the measurement. The most simple and convenient method of this study would be to determine the creep as a function of time after applying the constant stress to the film materials. The apparatus[2]

1) Presented at the Symposium of Colloid Chemistry of the Chemical Society of Japan, Nov. 1952, Fukuoka.

2) K. Inokuchi, This Bulletin, **23**, 500 (1953).

used in the previous paper, although it involves the determination of creep against time, was not satisfactory in achieving the quantitative analysis of the creep curve, since the stress was not kept constant during the test, but decayed with the creep. In fact, quantitative analysis of the data obtained with the previous apparatus becomes rather involved and often impractical, when the experiment is carried out with films, the rheological properties of which are more or less complicated. The desirable condition is that the stress remains constant throughout the creep test. In this paper, an apparatus useful under such condition is described.

Construction of Apparatus

The essential elements of the apparatus consist of a ring and a suspending wire similar to those used in the previous case. The torque applied to the ring is supplied from the distorsion of the wire. In order to realize the condition of constant stress, it is only necessary to maintain the twisted angle of the torsion wire, which is given at the beginning of the measurement, to be constant during the experiment. In the present apparatus, such mechanism is automatically conducted by a phototube relay system. The essential part is divided into the following two systems: (1) optical system, and (2) driving system.

(1) Optical System Fig. 1 illustrates the

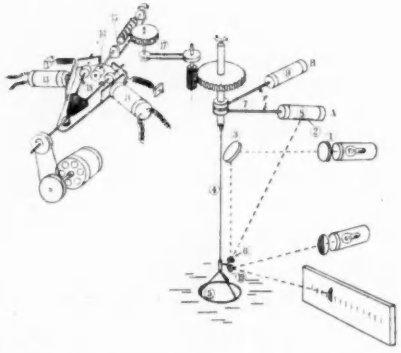

Fig. 1. Schematic view of the apparatus

schematic view of the apparatus. A beam of parallel light, passed through a condensing lens (1), is projected to the first mirror (3) which is fixed closely near the torsion wire with oblique inclination so that the light beam is made parallel to the torsion wire (4). The ring (5) provides a small concave mirror (6) of about 4 mm. in diameter which moves with the rotation of the ring. This second mirror (6) reflects a part of the parallel light from the first mirror (3) to form an intense light spot at a certain point within the plane determined by the wire (4) and the center of the mirror (6). Such a design of the optical system would enable the angular displacement of the light spot to be equal to that of the ring, because the projecting light is made parallel to the rotating axis of the mirror (6). Thus, if the driving of the torsion head is so conducted that it always moves together with the light spot, the condition of constant stress would be satisfied. The conduction mechanism of the torsion head is as follows.

The torsion head provides two rods (7) of about 15 cm. long, extending outwards at right angles to it, at each end of which phototube housings (8, 9) are attached respectively. These rods can be turned around the torsion head and be fixed at any position desired. Each of the housings encases two RCA-921 phototubes (A, B) respectively with each photosurface downwards. Each housing provides a narrow and long slit (2) of 2×40 mm. along the median line of its ventral side respectively, so that the photosurface can receive the light beam through the slit, when the position of the rod is properly adjusted.

(2) Driving System The driving of the torsion head is wholly conducted by a phototube relay system. The principal manner is as follows: as soon as a photosurface receives light, the driving system of the torsion head is so actuated that the head rotates toward one direction, whereas once the photosurface becomes dark, it is inversely actuated so that the head rotates toward the opposite direction. Such mechanism would render the torsion head a reciprocating motion about the light spot if the motion of the light spot is sufficiently slow compared with that of the torsion head. Such a function is quite similarly given to both phototubes (A) and (B), and the alternative use of these tubes, either (A) or (B), is achieved by the switch (10) (see Fig. 3).

The essential elements of the arrangement employed in the driving system are indicated in the functional block diagram of Fig. 2. The

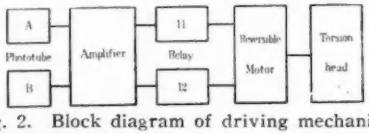

Fig. 2. Block diagram of driving mechanism using phototube relay.

two-step amplifier is ordinarily designed as illustrated in Fig. 3. The amplified photocurrent actuates the relays (11, 12) which transfer the photosignal to the reversible motor, which in turn drives the torsion head toward the alternative directions. Each of the relays (11, 12) is separately actuated by the phototubes (A) and (B), respectively, and the alternative use of them is also accomplished by the reversible switch (10). Each relay provides two contacts respectively, which intermit the rectified current for the reversible motor according to the following mechanism. Even when the relay is

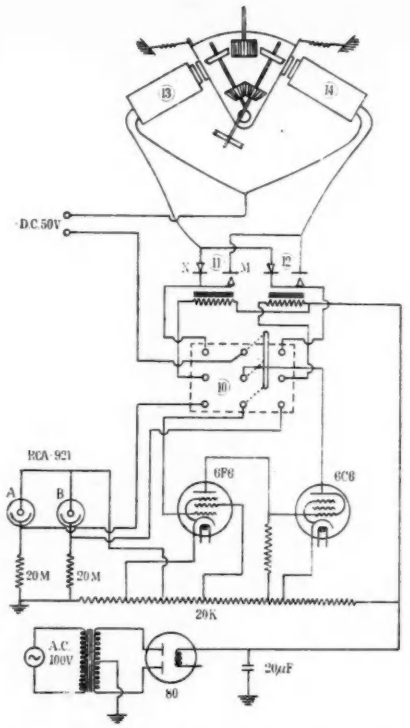

Fig. 3. Schematic circuit of phototube amdlifier

at rest, one of these contacts (for example, M) is closed by means of a spring, while another contact (N) is opened. Once the relay is actuated, however, the situation is inverted, that is, the contact (M) is opened, and (N) is closed. Since each contact is connected to the magnets (13, 14) of the reversible motor respectively, the reciprocating motion of the motor takes place according to whether or not the relay is actuated.

The construction of the reversible motor will be apparent when referred to Fig. 1 and 3. The gear shaft (15) with a friction rotor (16) is connected to the torsion head through the gear system (17). The reciprocating motion of the rotor is transmitted through the friction gear clutch assembly (18) which alternatively works by actuation of the magnet, either (13) or (14).

Principle of Operation

Suppose that the ring is allowed to touch the surface of the water covered with the film materials, being suspended by untwisted torsion wire, and the position of the phototube (A) is so adjusted that the photosurface just receives the light beam from the mirror (6) of the ring. If the switch (10) is so turned that the phototube (A) becomes active, and the phototube (B) is at rest, the torsion head would, according to the mechanism mentioned above, be driven toward one direction until the light spot is left outside of the slit of the phototube housing and accordingly the photosurface becomes dark, whereas once the surface becomes dark, the torsion head begins to return to the position where the light spot again enters into the slit. Here the situation becomes the same as at the beginning, and such to and fro motion further continues. In other words, the torsion head exercises a reciprocating motion about the light spot.

It must be mentioned here that the ring on the film, although suspended by a reciprocally twisted torsion wire, caused hardly perceptible reciprocating motion, but took a static position, so long as the amplitude as well as the period of the reciprocating motion of the torsion head was sufficiently small. Accordingly the film does not suffer any alternative shear in spite of the reciprocating motion of the torsion head. In the present apparatus, the frequency of the reciprocating motion was about 2–3 times per second and the amplitude of the motion was not more than 0.5 degree when the system was well adjusted.

Now let the second tube (B) be set by φ angles with respect of the first tube (A) and the switch (10) be so turned that the second tube (B) becomes active, leaving the first (A) at rest. Since, in this instance, the photosurface of the tube (B), which becomes newly active, remains still dark, the torsion head will be so driven until the second tube (B) catches the light spot. Here, the wire is twisted by φ. If the ring thereafter causes rotation owing to the stress imposed on it, the torsion head would also moves together with the moving light spot making a fine reciprocating motion about it, and the constant distortion of the wire will be maintained during the experiment.

At a later time, if the switch is returned to the original position so that the first tube (A) becomes active while the second (B) is at rest, the torsion head would inversely be driven so that the torsion of the wire is always set to the original state (zero). Such a condition would provide the curve of the after-effect of the testing film upon removal of the stress.

In the present study, where the motion of the ring in question was sufficiently slow compared with the rate of motion of the torsion head, there was no appreciable time lag of the head for pursuing the light spot, and the relative situation between the ring and the torsion head is considered to be constant throughout the experiment.

Performance

Briefly, the operation of the present apparatus is as follows. The ring is allowed to touch the clean surface of water. The phototubes are so set that the light spot from the mirror (6) just fits at the photosurface of the first tube (A) through the slit, and the second (B) is laid by φ angles with respect of the first (A). The testing film is now spread on the water surface. The position of the ring at respective time

is measured by means of a lamp and scale system using the mirror (19) attached to the ring. The switch (10) is so turned that only the tube (A) is active, being the tube (B) at rest, and the original position of the ring is marked on the scale. Then, in order to impose the stress on the ring, the switch (10) is changed so that only the tube (B) is active, leaving the tube (A) at rest, and the deflection of the ring is recorded with time. If a study of the after-effect upon removal of the stress is intended, it is enough to return the switch (10) to the original position.

The equations to calculate the surface shear modulus of rigidity (G) and surface viscosity coefficient (η) may be expressed as follows

$$G = \frac{k}{4\pi}\left(\frac{1}{r_1^2} - \frac{1}{r_2^2}\right)\frac{\varphi}{\theta} \qquad (1)$$

$$\eta = \frac{k}{4\pi}\left(\frac{1}{r_1^2} - \frac{1}{r_2^2}\right)\frac{\varphi}{\dot{\theta}} \qquad (2)$$

where r_1, r_2 are the radii of the ring and of the circular film coaxial to the ring, respectively, θ, the angular displacement of the ring, and k, the torsion constant.

Test and Results

The measured extent of coincidence between the rotating angles of the ring and the corresponding angles of the light spot was shown in Fig. 4. Fairly good coincidence

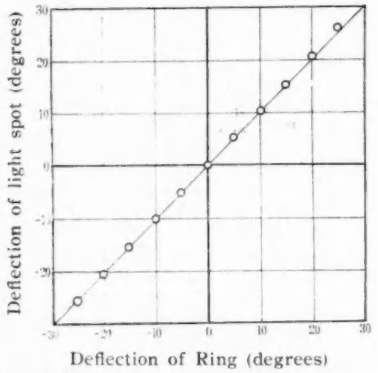

Fig. 4. Relation between rotating angles of the ring and the corresponding deflection angles of light spot.

was seen over the range of about 50 degrees within the error of a few per cent.

Fig. 5 shows the deformation-time curve ($\theta - t$ curve) of serum albumin monolayer determined with the present apparatus. Here, it was intended that the present apparatus was tested by being referred to the data obtained with the apparatus presented in a previous paper. Fig. 6 gives the $\theta - t$ curve together with the $\log(\varphi - \theta) - t$ plot when the previous apparatus was applied to the same film. From the linearity of $\log(\varphi - \theta) - t$ plot[3], it was found that this film behaves as a simple viscous matter of Newtonian nature. This fact predicts that the present apparatus would give a straight line to the $\theta - t$ plot if only the stress is kept constant during the test, in contrast with the droop curve in case of the previous apparatus. This prediction was verified in Fig. 5 in which good linearity was yielded in the $\theta - t$ plot. The basic requirement of this apparatus—constant stress—was found to be fulfilled within experimental error.

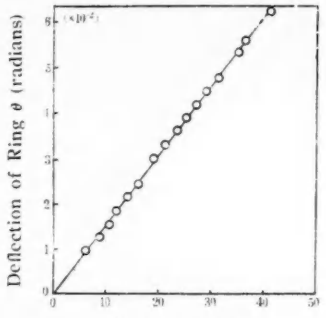

Fig. 5. $\theta - t$ plot of serum albumin monolayer determined by the present apparatus on 5% ammonium sulfate aqueous solution, surface area, 1.03 sq. m. per mg., temperature, 16°C.

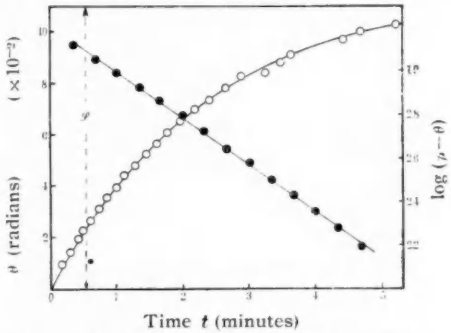

Fig. 6. $\theta - t$ curve (open circles) and $\log(\varphi - \theta) - t$ curve (full circles) of serum albumin monolayer, determined by the previous apparatus.

As an example of a less simple creep curve, a monolayer of ovalbumin film was subjected to our test. The deformation-time

3) V. E. Hatschek and R. S. Jane, *Koloid-z.* **39**, 300 (1926).

curve determined by the present apparatus was given in Fig. 7, where the experimental

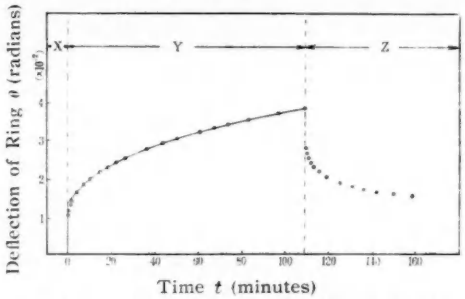

Fig. 7. $\theta-t$ curve for ovalbumin monolayer on 5% ammonium sulfate solution, surface area, 0.904 sq. m. per mg., temperature, 19°C. Full circles indicate the observed values, and solid line, the calculated curve. (X) represents the dead time, (Y), the time in which the stress was imposed, and (Z), the time, after the stress was removed.

conditions are indicated in the legend. From inspection of the shape of the curve, it will be apparent that the curve is characterized by instantaneous elastic response, retarded elastic response and irreversible flow. The solid curve represents the trace which was drawn according to the following well-known equation, putting the proper numerical values into the respective variables

$$\theta=\theta_0+A(1-e^{-t/\tau})+\lambda t \qquad (3)$$

where θ represents the angular displacement of the ring at time t, θ_0, an initial displacement of the ring due to an instantaneous elasticity, λ, the constant motion rate of the ring in viscous flow region, A, the final and maximum response due to a retarded elasticity, and τ, the retardation time. It was noted here that, except for the initial transcient creep region, the observed values were well expressible by such a simple equation. Putting θ_0, A, and λ into the equation (1) and (2), an instantaneous surface shear modulus of rigidity (G_1), a retarded surface shear modulus of rigidity (G_2), and surface viscosity coefficient (η) of the constant rate flow were calculated as follows: $G_1=2.7$ dynes/cm. $G_2=3.2$ dynes/cm., $\eta=2.1\times10^4$ dynes/cm./sec., and $\tau=21.7$ minutes.

Summary

A surface rheometer was presented which enables the creep of surface films to be measured under constant shear stress. The main construction consists of a ring and a suspending torsion wire. Automatic adjustment of the torsion head driving, which made distorsion of the wire to be constant throughout the creep test, was accomplished by means of a phototube relay mechanism. The creep curve and its analysis data of ovalbumin monolayer were also presented.

The author wishes to express his hearty thanks to Prof. T. Tachibana for his helpful advice and encouragement, and to Dr. J. Sakagami of the Department of Physics of this University for his valuable discussion concerning the construction of the apparatus.

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The Syntheses from Levulinic Acid. A Possible Use of Some 2 Methyl-5-oxopyrrolidine-2 carboxylic Esters as Plasticizers[1]

By Tadao TAKENISHI and Osamu SIMAMURA

(Received February 18, 1954)

The object of the present investigation is to search for possible uses as chemical intermediates of levulinic acid, which is often obtained in quantities as a by-product from carbohydrate materials in food industries. The application of the Strecker synthesis[2] to levulinic acid gave 2-amino-2-methylglutaric acid, from which several derivatives were prepared including 2-methyl-5-oxopyrrolidine-2-carboxylic acid. Since esters as a class are of general interest as plasticizers, some 2-methyl-5-oxopyrrolidine-2-carboxylic esters were prepared and those of higher alcohols were tested for plasticizer performance. They are compatible and efficient for

1) Part of the material of this report was presented at a meeting of the Chemical Society of Japan held on Oct. 2, 1952, at Niigata.

2) A. Strecker, *Ann.*, **75**, 27 (1850).

plasticizing vinyl chloride resin; with regard to heat stability, they are unsatisfactory only in one respect in that the plasticized sheets of polyvinyl chloride, heated at 110° for six hours, became colored light brownish violet. The results are recorded in the accompanying table.[3]

PROPERTIES OF POLYVINYL CHLORIDE SHEETS PLASTICIZED WITH 2-METHYL-5-OXOPYRROLIDINE-2-CARBOXYLIC ESTERS

	n-Octyl Ester		2-Ethylhexyl Ester		Dodecyl Ester	
Plasticizer (parts for 100 parts polyvinyl chloride with 2 parts lead stearate)	30	50	30	50	30	50
Modulus at 100% Elongation, kg./cm².	157	64	153	65	200	82
Elongation, %	268	305	263	335	275	315
Tensile Strength, kg./cm².	282	192	300	208	322	205
Tear Resistance, kg./cm.	118	74	140	82	136	78
Oil Extraction (*a*)	—	10.78	—	5.32	—	15.05
Water Extraction(*b*)	—	5.83	—	3.91	—	0.20
Low Temperature Flexibility(*c*)	—	9.30	—	13.27	—	7.65

(*a*) % gasoline-soluble substances, at 18~23°, for 24 hrs.
(*b*) % water-soluble substances, at 50°, for 24 hrs.
(*c*) Elongation at 25~26° / Elongation at −4 to −5°.

Experimental

2-Amino-2-methylglutaric Acid A solution of 102 g. (1.9 moles) of ammonium chloride in 240 cc. of lukewarm water was added, followed by 120 cc. (1.7 moles) of 28% ammonium hydroxide, to a solution of 86 g. (1.7 moles) of sodium cyanide in 170 cc. of water placed in a round-bottomed flask fitted with a ground-glass stopper. The mixture was stirred while 200 g. (1.7 moles) of ammonium levulinate in aqueous solution was added. The flask was then stoppered, the stopper secured firmly by means of adhesive tape, and the flask kept half immersed for six hours in a water bath at 65~70°. The reaction mixture was then cooled, poured into 2 l. of concentrated hydrochloric acid contained in a round-bottomed flask cooled by a stream of water, and the mixture saturated with hydrogen chloride. After standing overnight, it was refluxed for three hours to hydrolyze the acid amide produced. After cooling, the precipitated inorganic salts were filtered off on a Büchner funnel. The filtrate was concentrated under reduced pressure on a water bath, and the deposited inorganic salts were filtered. When the filtrate was neutralized to a pH 3.2 with aqueous sodium hydroxide and the inner wall of the vessel scratched vigorously, 2-amino-2-methylglutaric acid separated in fine crystals, which were collected on a Büchner funnel. The yield of the product was 210 g. (70% of the theoretical amount). This crude amino acid was dissolved in hot water, charcoaled and filtered, giving fine crystalline product, m.p. 170° (Found: C, 44.73; H, 6.88; N, 8.69. Calcd. for $C_5H_{11}O_4N$: C, 44.10; H, 7.20; N, 8.23%).

2-Benzamido-2-methylglutaric Acid Benzoyl chloride (6.2 g.) was added to 2-amino-2-methylglutaric acid (8 g.) dissolved in a solution of 6.5 g. of sodium hydroxide in water, the mixture shaken for 30 minutes, acidified with hydrochloric acid, the precipitated benzoic acid filtered off, the filtrate concentrated to half the original volume, extracted with ether and ethyl acetate, the combined extracts dried over anhydrous sodium sulfate, and the solvent removed on a water bath. Recrystallization of the residue from aqueous alcohol gave the benzoyl derivative, m.p. 196~7° (Found: N, 5.45; neutralization equiv., 132.5. Calcd. for $C_{13}H_{15}O_5N$: N, 5.28%; neutralization equiv., 132.5.).

2-Acetamido-2-methylglutaric Anhydride 2-Amino-2-methylglutaric acid (8 g.) was refluxed with 20 cc. of acetic anhydride and 15 cc. of acetic acid for 4 hours. After the excess of acetic anhydride was decomposed with water, the mixture was concentrated in vacuo and the remaining oil was induced to crystallize by rubbing with ethyl acetate, giving 2-acetamido-2-methylglutaric anhydride, m.p. 141~2° (from ethyl acetate) (Found: N, 7.71. Calcd. for $C_8H_{11}O_4N$: N, 7.58%).

2-Acetamido-2-methylglutaric Acid To 8 g. of 2-amino-2-methylglutaric acid and 25 cc. of acetic anhydride, aqueous sodium hydroxide was added drop by drop with vigorous shaking until the mixture was alkaline. After shaking for thirty minutes, the mixture was neutralized with hydrochloric acid, concentrated in vacuo, the precipitated inorganic salts filtered off, the

3) The authors are indebted to Mr. S. Takazawa of Yamato Rubber Works, Tokyo, for the performance data.

filtrate concentrated to dryness in vacuo, and the residue triturated with ethyl acetate and filtered off, giving crude crystals melting at 126~135°. An analytically pure sample was prepared by repeated crystallization from water, m.p. 182~3° (Found: N, 6.76; neutralization equiv., 110.5. Calcd. for $C_8H_{13}O_5N$: N, 6.89%; neutralization equiv., 101.5).

Diethyl 2-Amino-2-methylglutarate The diethyl ester was prepared by Fischer's method[4]. 2-Amino-2-methylglutaric acid (20 g.) was heated on a water bath with 120 cc. of absolute ethanol which had previously been saturated with dry hydrogen chloride until all the amino acid dissolved, and the heating was continued for a further five hours. The mixture was then concentrated under diminished pressure, added with 100 cc. of ethanol saturated with dry hydrogen chloride, heated and concentrated as above, the whole cycle of procedures being repeated three times. The oily product thus obtained was dissolved in a small amount of water, the solution neutralized and the ester extracted several times with ether. The combined ether extracts were dried over sodium sulfate, evaporated, and the residue distilled in vacuo, giving 7 g. of diethyl ester, b.p. 102~4° at 0.5 mm. Hg, d_4^{20} 1.0550, n_D^{20} 1.4428 (Found: N, 6.45; MR_D, 54.56. Calcd. for $C_{10}H_{19}O_4N$: N, 6.45%; MR_D, 55.11.).

2-Methyl-5-oxopyrrolidine-2-carboxylic Acid 2-Amino-2-methylglutaric acid was dehydrated to 2-methyl-5-oxopyrrolidine-2-carboxylic acid by heating at 180~200° in a practically quantitative yield, m.p. 144~5° (from hot water) (Found: N, 9.78; neutralization equiv., 143. Calcd. for $C_5H_9O_3N$: N, 9.86%; neutralization equiv., 143.).

Ethyl 2-Methyl-5-oxopyrrolidine-2-carboxylate 2-Methyl-5-oxopyrrolidine-2-carboxylic acid (15 g.), 150 cc. of ethanol, 200 cc. of benzene and 1 cc. of concentrated sulfuric acid were heated in a round-bottomed 1 l. flask fitted with a refluxing condenser and separator so arranged that the upper layer of the condensing liquid containing benzene and ethanol was returned to the reaction flask and the lower water layer withdrawn from time to time. The flask was heated until no further separation of water occurred. The solvent was removed from the reaction mixture in vacuo, the residue dissolved in ether, the ether solution washed with aqueous solution of sodium bicarbonate, the ether removed, the residue subjected to fractional distillation under reduced pressure, giving 10 g. of ethyl ester, colorless liquid, b.p. 126~130° at 0.5 mm. Hg, d_4^{20} 1.1283, n_D^{20} 1.4690 (Found: N, 8.39; MR_D, 43.24, Calcd. for $C_8H_{13}O_3N$: N, 8.18%; MR_D, 42.21.).

Butyl 2-Methyl-5-oxopyrrolidine-2-carboxylate This ester was prepared from 2-methyl-5-oxopyrrolidine-2-carboxylic acid similarly to the ethyl ester in 95% yield, b.p. 141~2° at 0.5 mm. Hg (Found: N, 7.05. Calcd. for $C_{10}H_{17}O_3N$: N, 7.03%.). It was also synthesized from 2-amino-2-methylglutaric acid by the same procedure in 80% yield, b.p. 141~2° at 0.5 mm. Hg, d_4^{20} 1.0698, n_D^{20} 1.4676 (Found: N, 7.13; MR_D, 51.68. Calcd. for $C_{10}H_{17}O_3N$; N, 7.03%; MR_D, 51.45.).

Octyl, 2-ethylhexyl, dodecyl and benzyl esters were prepared from 2-methyl-5-oxopyrrolidine-2-carboxylic acid by the same procedure as above.

Occtyl 2-Methyl-5-oxopyrrolidine-2-carboxylate (yield 75%), b.p. 173~4° at 1.0 mm. Hg, d_4^{20} 1.0062, n_D^{20} 1.4652 (Found: N, 5.63; MR_D, 70.29, Calcd. for $C_{14}H_{25}O_3N$: N, 5.48%; MR_D, 69.80.).

2-Ethylhexyl 2-Methyl-5-oxopyrrolidine-2-carboxylate (yield 85%), b.p. 179~181° at 3.0 mm. Hg, d_4^{20} 1.0106, n_D^{20} 1.4668 (Found: N, 5.48; MR_D, 70.29. Calcd. for $C_{14}H_{25}O_3N$: N, 5.48%; MR_D, 69.80.).

Dodecyl 2-Methyl-5-oxopyrrolidine-2-carboxylate (yield 50%), b.p. 198~199° at 0.5 mm. Hg, m.p. 37~9° (from ethanol) (Found: N, 4.47. Calcd. for $C_{18}H_{33}O_3N$: N, 4.49%.).

Benzyl 2-Methyl-5-oxopyrrolidine-2-carboxylate (yield 70%), b.p. 237~240° at 1 mm. Hg, m.p. 94~95° (from carbon tetrachloride) (Found: N, 6.01. Calcd. for $C_{13}H_{15}O_3N$; N, 6.00%.).

Summary

The synthesis of 2-amino-2-methylglutaric acid from levulinic acid by Strecker's method is reported. This acid gives 2-methyl-5-oxopyrrolidine-2-carboxylic acid on dehydration, and some of its esters were prepared and tested for plasticizer performance.

The authors are indebted for generous supplies of materials to the Management of Sanko Co., Tokyo, to which the thanks of T.T. are also due for leave of absence to participate in this work.

Department of Chemistry, Faculty of Science, Tokyo University

4) E. Fischer, *Ber.*, **34**, 433 (1901).

The Condensations of Furfural with Methyl Isobutyl Ketone and Phenylacetone by Aqueous Sodium Hydroxide

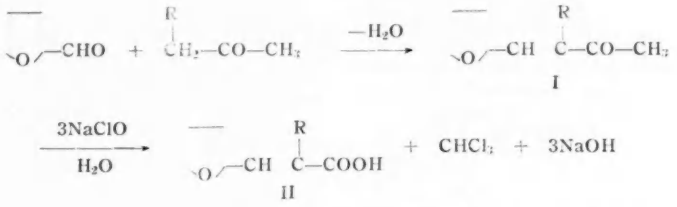
By Hiroshi MIDORIKAWA

(Received February 23, 1954)

In the previous reports[1] were represented the following facts: At the lowered reaction temperature 0–5°, methyl ethyl ketone tends to condense with furfural or benzaldehyde by alkali at its α-methylene group, and methyl propyl ketone, though slightly, has such a tendency in the condensation with furfural by alkali. At the elevated reaction temperature 60–65°, methyl ethyl ketone, as well as methyl propyl ketone, condenses with furfural chiefly at their α-methyl groups. In the condensation with benzaldehyde at the elevated reaction temperature 60–65°, methyl ethyl ketone reacts exclusively at its α-methyl group.

The present work consists in studying whether methyl isobutyl ketone and phenylacetone, on the condensation with furfural by aqueous sodium hydroxide, react at their α-methylene groups or not. In the reaction of furfural with methyl isobutyl ketone by alkali, there are few reports[2,3,4]. But those appear to have no such consideration.

When the condensation of furfural with the ketone $CH_3—CO—CH_2—R$ takes place at its α-methylene group, the resulting furfurylidene ketone (I) must be oxidised by sodium hypochlorite to α-R-2-furanacrylic acid (II), as in all cases so far examined[1]. The reaction is represented in the following formulae.



On the condensation of furfural with methyl isobutyl ketone by aqueous sodium hydroxide, both condensation products at the lowered and at the elevated reaction temperatures gave only one species (m.p. 177–178°) of semicarbazone, which was considered to be identical with the semicarbazone (m.p. 175–176°) of the condensation product obtained by Wienhaus and Leonhardi[3]. On suspension of these condensation products in sodium hypochlorite solution for 2 days with occasional shaking, no α-isopropyl-2-furanacrylic acid and no smell of chloroform were detected. Consequently, it seemed certain that the condensation products were composed of 1-(2-furyl)-5-methyl-1-hexen-3-one (III) resulting from the condensation of furfural at the α-methyl group of methyl isobutyl ketone irrespective of the reaction temperatures, as illustrated below.

This semicarbazone (m.p. 177–178°) was converted into two species of 2,4-dinitrophenylhydrazone. One was reddish-orange, flat-tened needles (m.p. 196–197°) and the other red, long needles (m.p. 144–145°). These two forms also were directly obtained from both the condensation products at the lowered and elevated reaction temperatures. Furthermore, it was of interest that the red, long needles shifted readily to the reddish-orange needles in dilute alcoholic sulfuric acid. Probably, these two forms of 2,4-dinitrophenylhydrazone may be the syn- and antiisomers as two *o*-tolyhydrazones of N-phenacyl-*p*-anisidine.[5]

Refluxion of the condensation product at the reaction temperature 60–65° with alcoholic hydrochloric acid and subsequent hydrolysis gave a dioxocarboxylic acid (m.p. 79–80°) in a good yield, which was considered to be γ,ζ-dioxo-ϑ-methylcapric acid (IV), as reported by Breusch and Ulusoy[4]. The reaction sequence is illustrated in the accompanying formulae.

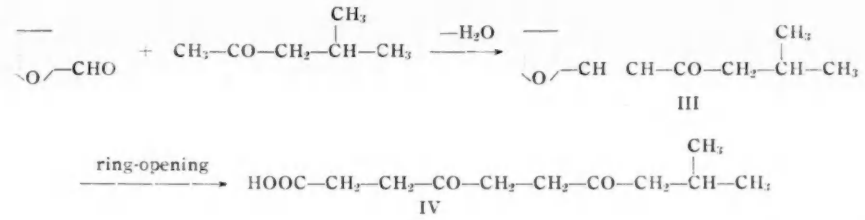
1) H. Midorikawa, This Bulletin, **26**, 160 (1953); **27**, 131 (1954), **27**, 143 (1954); **27**, 149 (1954).

2) J. T. Thurston, *C. A.*, **33**, 5023 (1945); H. Wachs and O. F. Hedenburg, *J. Am. Chem. Soc.*, **70**, 2695 (1948).

3) H. Wienhaus and H. Leonhardi, *C. A.*, **24**, 2127 (1930).

4) F. L. Breusch and E. Ulusoy, *C. A.*, **42**, 5850 (1948).

5) M. Busch, G. Friedenberger and W. Tischbein, *Ber.*, **56**, 999 (1926).



III

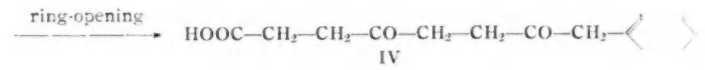
IV

Phenylacetone was also condensed with furfural at the lowered and elevated reaction temperatures, 5° and 60–70°. Neither of the condensation products at the lowered and elevated reaction temperatures, on sodium hypochlorite oxidation, gave any α-phenyl-2-furanacrylic acid nor any smell of chloroform. It seemed certain that the condensation of phenylacetone with furfural gave 4-(2-furyl)-1-phenyl-3-buten-2-one (V), reacting at the α-methyl group of the ketone irrespective of the reaction temperatures, as illustrated below.

On the other hand, both condensation products at the lowered and elevated reaction temperatures gave two species of semicarbazone, colourless prisms (m.p. 210–212°) and colourless prisms (m.p. 163–164°), which were converted respectively into 2,4-dinitrophenylhydrazones of red, flattened needles (m.p. 183–184°) and reddish-orange leaflets (m.p. 178–179°). The condensation product at the elevated reaction temperature gave these two semicarbazones in equal proportions, and the condensation product at the lowered reaction temperature gave the semicarbazone of prisms (m.p. 210–212°) chiefly.

Moreover, both condensation products at the lowered and elevated temperatures afforded a dioxocarboxylic acid in nearly equal yields on the ring-opening in alcoholic hydrochloric acid, which was considered to be γ,ζ-dioxo-η-phenylcaprylic acid (VI). From these results, it may be supposed that the compound (V) obtained here consists of the cis- and trans-isomers. The reaction sequence is illustrated by the following formulation.

V



IV

Ultimately, methyl isobutyl ketone and phenylacetone appeared difficult to condense with furfural at their α-methylene groups, in contrast with methyl ethyl ketone and methyl propyl ketone. This fact may perhaps be attributed to the presence of the bulky group adjacent to the α-methylene group of these ketones, such as isopropyl and phenyl groups.

Experimental

Condensation of Methyl Isobutyl Ketone with Furfural Into a stirred suspension of furfural (15 g.) and methyl isobutyl ketone (30 g.) in water (200 cc.) was at once introduced 5% aqueous sodium hydroxide (10 cc.) at 60°, with stirring. After prolonged stirring for 2 hrs. at 60–65°, the reaction mixture was neutralised with dilute hydrochloric acid and the oily layer separated. The aqueous solution was extracted twice with ether and the ether extract combined with the oil. Fractionation of the ether solution gave a yellow oil (12.7 g.) distilling at 124–126°/6 mm., which was considered to consist of 1-(2-furyl)-5-methyl-1-hexen-3-one (III), $C_{11}H_{14}O_2$. (Found: C, 73.84; H, 7.61%; Calcd. for $C_{11}H_{14}O_2$: C, 74.11; H, 7.96%).

This fraction gave a semicarbazone crystallising from methanol-water as colourless needles, (m.p. 177–178°; lit[3]., m. p. 175~176°.) (Found: C, 61.09; H, 6.94; N, 17.65%; Calcd. for $C_{12}H_{17}O_2N_3$: C, 61.24; H 7.29; N, 17.86%).

This fraction gave nearly equal amounts of two 2,4-dinitrophenylhydrazones, reddish-orange, flattened needles (m.p. 196–197°) and red, long needles (m.p. 145–146°). The former 2,4-dinitrophenylhydrazone was comparatively sparingly soluble in pyridine and the latter fairly soluble in pyridine. Those isomers were separated by the solubility difference. Needles (m.p. 196–197°) (Found: C, 57.09; H, 4.79; N, 15.22%; Calcd. for $C_{17}H_{18}O_5N_4$: C, 56.96; H, 5.07; N, 15.63%). Needles (m.p. 145–146°) (Found: C, 57.12; H, 4.74; N, 15.50%; Calcd. for $C_{17}H_{18}O_5N_4$: C, 56.96; H, 5.07; N, 15.63%).

The latter needles (m.p. 145–146°) were readily transformed into the former (m.p. 196–197°), being suspended in hot dilute methanolic sulfuric acid for a short time.

The semicarbazone (m.p. 177–178°) was also converted into a mixture of these two 2,4-dinitrophenylhydrazones, reacting with 2,4-dinitrophenylhydrazine in alcoholic sulfuric acid.

The condensation of furfural with methyl isobutyl ketone at the reaction temperature 0–5° was carried out by stirring a mixture of furfural (15 g.), methyl isobutyl ketone (30 g.), water (250 cc.) and 10% aqueous sodium hydroxide (30 cc.) for 6 hrs. The reaction mixture was worked up in the same manner as in the case of the foregoing condensation, and a fraction (20 g.) distilling at 121–124°/5 mm. was collected. This fraction also gave the same semicarbazone and 2,4-dinitrophenylhydrazones as in the case of the condensation at the reaction temperature 60–65°.

Both condensation products at the reaction temperatures, 60–65° and 0–5° were suspended in the sodium hypochlorite solution[6], but no heat was generated and no α-isopropyl-2-furanacrylic acid detected.

Condensation of Furfural with Phenylacetone Furfural (15 g.) and phenylacetone (30 g.) were suspended in water (200 cc.), and 5% aqueous sodium hydroxide was at once run in at about 60° with stirring. After prolonged stirring for 5.5 hrs. at 60–70°, the reaction mixture was worked up in the same manner as in the foregoing condensation, and a fraction (22 g.) distilling at 172–177°/5 mm. was obtained, which was considered to be 4-(2-furyl)-1-phenyl-3-buten-2-one (V), $C_{14}H_{12}O_2$. (Found: C, 78.71; H, 5.69%; Calcd. for $C_{14}H_{12}O_2$: C, 79.28; H, 5.71%).

This fraction afforded nearly equal amounts of two semicarbazones, colourless prisms (m.p. 163–164°) fairly soluble in methanol and colourless needles(m.p. 210–212°)sparingly soluble in methanol. These isomers were separated by the solubility difference. Prisms (m.p. 163–164°)(Found: C, 66.48; H, 5.50; N, 15.45%; Calcd. for $C_{15}H_{15}O_2N_3$: C, 66.88; H, 5.62; N, 15.61%). Needles (m.p. 210–212°) (Found: C, 66.68; H, 5.61; N, 15.43%; Calcd. for $C_{15}H_{15}O_2N_3$: C, 66.88; H, 5.62; N, 15.61%).

The former semicarbazone was converted to a 2,4-dinitrophenylhydrazone crystallising from pyridine as reddish-orange, lustrous leaflets (m.p. 178–179°), and the latter semicarbazone to a 2,4-dinitrophenylhydrazone crystallising from pyridine as red, flattened needles (m.p. 183–184°). Orange leaflets (m.p. 178–179°) (Found: C, 60.90; H, 4.04; N, 13.94%; Calcd. for $C_{20}H_{16}O_5N_4$: C, 61.20; H, 4.12; N, 14.28%). Red, flattened needles (m.p. 183–184°) (Found: C, 60.88; H, 4.03; N, 14.17%; Calcd. for $C_{20}H_{16}O_5N_4$: C, 61.20; H, 4.12; N, 14.28%).

Furfural (15 g.) and phenylacetone (30 g.) were suspended in a mixture of alcohol (50 cc.) and water (250 cc.), whereupon 10% aqueous sodium hydroxide was run in at about 5° with stirring. After prolonged stirring for 6.5 hrs. at 5°, the reaction mixture was worked up as described above, and a fraction (8 g.) distilling 170–178°/5 mm. obtained. This fraction gave the red flattened needles (m.p. 183–184°) mainly.

Both condensation products at the reaction temperatures 60–70° and 5° were suspended in the sodium hypochlorite[6], but no heat was generated and no α-phenyl-2-furanacrylic acid detected.

Ring-opening The condensation product (III) (2 g.) of furfural with methyl isobutyl ketone at the reaction temperature 60–65° was refluxed with conc. hydrochloric acid (1.5 cc.) and alcohol (5 cc.) on the water-bath for 3 hrs. The reaction mixture, after addition of an equal volume of dilute hydrochloric acid, was evaporated to dryness on the water-bath. The residue was extracted with a sufficient quantity of water, and the extract evaporated on the water-bath to give an oily matter which on cooling formed a crystalline mass (1 g.). It was recrystallised from ligroin as colourless leaflets, m.p. 79–80°. This specimen was considered to be γ,ζ-dioxo-ϑ-methylcapric acid (IV)[4], $C_{11}H_{18}O_4$. (Found: C, 61.57; H, 8.23%; Calcd. for $C_{11}H_{18}O_4$: C, 61.64; H, 8.47%).

The condensation product (V) (2 g.) of furfural with phenylacetone at the reaction temperature 60–70° was refluxed with conc. hydrochloric acid (1.5 cc.) and alcohol (5 cc.) for 3 hrs. The reaction mixture, after being worked up as described above, gave a crystalline mass (0.3 g.), which was recrystallised from ligroin-ethyl acetate as colourless rhombic plates, m.p. 88–89°.

By the same procedure, the condensation product (V) (2 g.) of furfural with phenylacetone at the reaction temperature 0–5° yielded the same crystals (0.3 g.). This specimen was considered to be γ,ζ-dioxo-η-phenylcaprylic acid (VI), $C_{14}H_{18}O_4$. (Found: C, 67.37; H, 6.62%; Calcd. for $C_{14}H_{18}O_6$: C, 67.71; H, 6.49%).

Summary

Methyl isobutyl ketone and phenylacetone, unlike methyl ethyl ketone[1], condensed with furfural by sodium hydroxide at their α-methyl groups irrespective of the reaction temperature, giving 1-(2-furyl)-5-mthyl-1-hexen-3-one (III) and 4-(2-furyl)-1-phenyl-3-buten-2-one (V) respectively.

1-(2-Furyl)-5-methyl-1-hexen-3-one (III) gave the two forms of 2,4-dinitrophenylhydrazone. One (m.p. 145–146°) shifted readily to the other (m.p. 196–197°) in dilute alcoholic sulfuric acid, and those may be the syn- and anti-isomers.

4-(2-Furyl)-1-phenyl-3-buten-2-one (V) obtained here gave the two species of semicarbazone which were converted into the respective two species of 2,4-dinitrophenylhydrazone. It may perhaps be composed of the cis- and trans-isomers. This furfurylidene ketone gave γ,ζ-dioxo-η-phenylcaprylic acid (VI) by the ring-opening in alcoholic hydrochloric acid.

The author expresses his sincere thanks to Dr. T. Hayashi for his kind advice.

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6) H. Midorikawa, This Bulletin, **26**, 462 (1953).

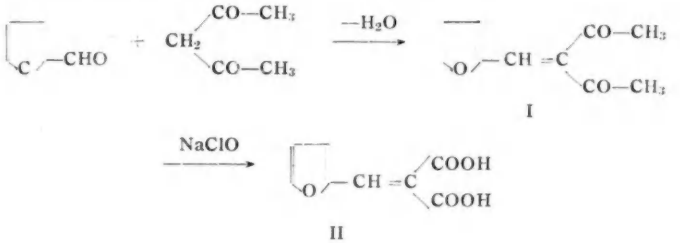
The Condensations of Furfural with Acetylacetone and Ethyl Propionylacetate

By Hiroshi MIDORIKAWA

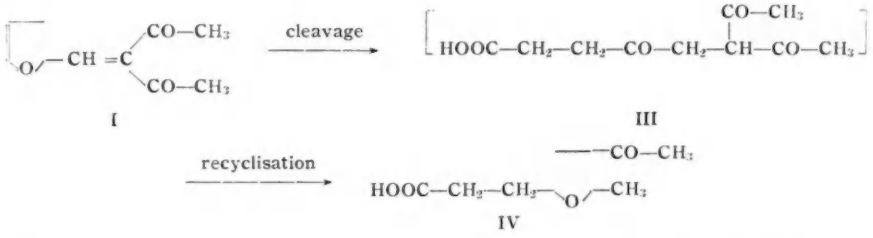
(Received February 23, 1954)

In the present paper were tried the condensations of furfural with acetylacetone and ethyl propionylacetate which have a reactive methylene group. In these cases, piperidine was a more suitable condensing agent than alkali, as in the condensation of ethyl acetoacetate with benzaldehyde[1] or furfural[2].

The condensation of furfural with acetylacetone by piperidine or aqueous sodium hydroxide gave 3-acetyl-4-(2-furyl)-3-buten-2-one (I), which was oxidised by sodium hypochlorite to furfurylidenemalonic acid (II). The reaction sequence is shown in the following formulae.



Furthermore, by refluxing with alcoholic hydrocnloric acid and subsequent hydrolysis, 3-acetyl-4-(2-furyl)-3-buten-2-one (I) gave an acid, $C_{10}H_{12}O_4$, which gave a semicarbazone, $C_{11}H_{15}O_4N_3$. It was infered that this acid did not possess the group $-CH(COCH_3)_2$ and the ordinary unsaturated nature, because it did not colorise aqueous ferric chloride and did not decolorise bromine water. Consequently, this compound $C_{10}H_{12}O_4$ was considered to be β-(4-acetyl-5-methyl-2-furyl)-propionic acid (IV) which was given by the ring-cleavage of the furfurylidene ketone (I) and the subsequent recyclisation[3] of the resulting cleavage product (III) with loss of water, as illustrated below. The analogous examples had already been reported with respect to furfurylidene-ethyl phenyl ketone[4] and furfurylidene-(3-methyl-4-methoxy-6-chloroacetophenone)[5].

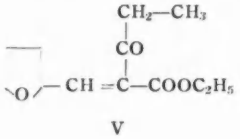


In this case the saturated cleavage product (III) was not isolated. The related furan (IV) obtained here showed no remarkable pine-splint reaction.

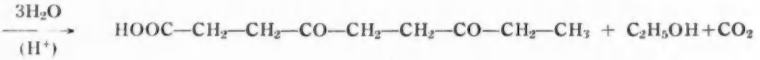
On the condensation of furfural with ethyl propionylacetate by piperidine was obtained ethyl α-propionyl-2-furanacrylate (V). This compound (V) yielded a dioxocarboxylic acid $C_9H_{14}O_4$ (m. p. 83–84°) on refluxing with alcoholic hydrochloric acid and subse-

1) E. Knoevenagel and W. Ruschhaupt, *Ber.*, **30**, 1026 (1898).
2) E. Knoevenagel, *Ber.*, **23**, 172 (1896).
3) A. P. Dunlop and F. N. Peters, "The Furans," p. 653, New York, Reinhold Publishing Corp., (1953).
4) D. L. Turner, *J. Am. Chem. Soc.*, **71**, 612 (1949).
5) R. H. Martin and R. Robinson, *J. Chem. Soc.*, 497 (1953).

quent hydrolysys. The present author* had already investigated that ethyl α-acetyl-2-furanacrylate yielded γ,ζ-dioxocaprylic acid by the same procedure. It was certain, therefore, that this dioxocarboxylic acid was γ, ζ-dioxopelargonic acid (VI), as illustrated by the following formulation.

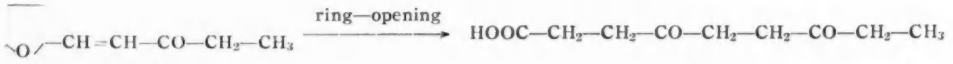


V



VI

In the preceding report[6], two furfurylidene ketones were obtained on the condensation of furfural with methyl ethyl ketone by alkali. One (b. p. 126°/19 mm.) of those, which gave the two forms of semicarbazone, needles (m. p. 183~184°) and plates (m. p. 166~167°), and the carmine needles (m. p. 206~207°) of 2, 4-dinitrophenylhydrazone, had been considered to be 1-(2-furyl)-penten-3-one (VII), owing to there being no reaction with sodium hypochlorite. The dioxocarboxylic acid (m. p. 83~84°) arising from this furfurylidene ketone on the ring-opening in alcoholic hydrochloric acid, which had been expected to be γ, ζ-dioxopelargonic acid, showed no depression on admixture with the authentic specimen (VI) obtained from ethyl α-propioyl-2-furanacrylate (V). Therefore, the considerations in the preceding paper were confirmed. The reaction sequence is illustrated by the accompanying formulation.



V VI

Experimental

3-Acetyl-4-(2-furyl)-3-buten-2-one (I). To a mixture of furfural (7 g.) and acetylacetone (7 g.) was added piperidine (0.1 g.) and the vessel was immersed in water at ordinay temperature for 2 days. The reaction mixture was extracted with ether. The ether extract, washed with dilute hydrochloric acid, was dried over calcium chloride. Fractionation of the ethereal solution gave a pale yellow, viscous oil (9 g.) distilling at 128~129°/4 mm., which solidified on standing for a short time. It formed colourless prisms on two recrystallisations from ether, m. p. 58~59°, which was the required ketone (I), $C_{10}H_{10}O_3$. (Found; C, 67.95; H, 5.65 %; Calcd. for $C_{10}H_{10}O_3$: C, 67.37; 5.66 %).

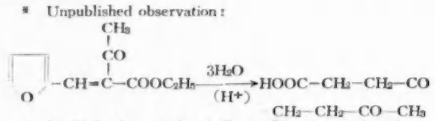
Its mono-2,4-dinitrophenylhydrazone formed lustrous, carmine prisms melting at 224~225° on crystallisation from pyridine. (Found: C, 53.72; H, 4.06; N, 15.27 %; Calcd. for $C_{15}H_{14}O_6N_4$; C, 53.61; H, 3.94; N, 15.61 %).

3-Acetyl-4-(2-furyl)-3-buten-2-one (I) (1 g.) was suspended in the sodium hypochlorite solution[6] (15 cc.) and the vessel immersed in water at ordinary temperature for 2 days, with occasional shaking. The reaction mixture was acidified with dilute hydrochloric acid and extracted twice with ether. The ether extract on evaporation gave colourless prismatic crystals (2 g.), which were recrystallised from acetic acid as colourless prisms melting at 206° with decomposition. This specimen was identical with furfurylidenemalonic acid (II), $C_8H_6O_5$; lit.,[7] m. p. 205°. (Found: C, 52.64; H, 3.32%; Calcd. for $C_8H_6O_5$: C, 52.73; H, 3.32 %).

3-Acetyl-4-(2-furyl)-3-buten-2-one (I) (2 g.) was refluxed with conc. hydrochloric acid (1.5 cc.) and alcohol (5 cc.) on the water-bath for 3 hrs. The reaction mixture, after the addition of an equal volume of dilute hydrochloric acid, was evaporated to dryness on the water-bath. The residue was extracted with a sufficient quantity of water, and the extract decolourised by active charcoal. Concentration of the solution on the water-bath gave faintly yellow needle crystals (0.1 g.), which recrystallised from ligroin-ethyl acetate, m. p. 125~126°; soluble in alcohol, benzene and acetone; sparingly soluble in ether. This specimen was considered to be β-(4-acetyl-5-methyl-2-furyl)-propionic acid (IV). (Found: C, 61.21; H, 6.03 %; Calcd. for $C_{10}H_{12}O_4$: C, 61.19; H, 6.16 %). Molecular weight: Found (Micro-Rast): 198; Calcd. for $C_{10}H_{12}O_4$: 196.

This acid gave a semicarbazone which formed colourless minute crystals (m. p. 206~207°); spar-

* Unpublished observation:



6) H. Midorikawa, This Bulletin, **25**, 460 (1953); **27**, 149 (1954).

7) C. Liebermann, *Ber.*, **27**, 287 (1894).

ingly soluble in methanol. (Found: C, 52.09; H, 5.95; N, 16.53%; Calcd. for $C_{11}H_{15}O_4N_3$: C, 52.15; H, 5.97; N, 16.59%).

The condensation of furfural with acetylacetone by alkali was also carried out at O°. From the reaction mixture was obtained a pale yellow, viscous oil distilling at 127~135°/3 mm., in a poor yield. This oil did not solidify on standing, but gave the same reaction products as in the case of the condensation product by piperidine—the 2,4-dinitrophenylhydrazone melting at 224~225°, furfurylidenemalonic acid (II) by sodium hypochlorite oxidation and β-(4-acetyl-5-methyl-2-furyl)-propionic acid (IV) on refluxing with alcoholic hydrochloric acid.

Ethyl α-propionyl-2-furanacrylate (V). Into a mixture of furfural (7 g.) and ethyl propionylacetate(10 g.) synthesised by Blaise's method[8] were introduced five drops of piperidine at −15°. After standing for 24 hrs. at −15~5°, five drops of pideridine were added to the mixture, and whole kept at −15~5° for 2 days. The reaction mixture was extracted with ether. The ether extract was washed with dilute hydrochloric acid and dried over calcium chloride. Fractionation of the ether solution gave a pale yellow oil (5 g.) distilling at 147°/5 mm., which solified on standing. This fraction recrystallised from ether-ligroin as colourless prisms, m. p. 57~58°. (Found: C, 64.70; H, 6.10%; Calcd. for $C_{12}H_{14}O_4$: C, 64.83; H, 6.35%).

Its 2,4-dinitrophenylhydrazone crystallised from pyridine as scarlet, fibrous needles, m. p. 223~224°. (Found: C, 53.40; H, 4.34; N, 13.81%; Calcd. for $C_{18}H_{18}O_7N_4$: C, 53.71; H, 4.51; N, 13.92%).

γ,ζ-Dioxopelargonic Acid (V). Ethyl α-propionyl-2-furanacrylate (V) (2 g.) was refluxed with conc. hydrochloric acid (2 cc.) and alcohol (5 cc.) on the water-bath for 5 hrs. The reaction mixture, after addition of an equal volume of dilute hydrochloric acid, was evaporated to dryness on the water-bath. The residue was extracted with hot water, and the extract was concentrated on the water-bath to yield a crystalline mass (0.2 g.) of the required acid. It was recrystallised from ligroin-ethyl acetate as colourless leaflets, m. p. 83~84°. (Found: C, 57.30; H, 7.28%; Calcd. for $C_9H_{14}O_4$: C, 58.03; H, 7.59%.).

This acid showed no depression of the mixed melting point with the dioxocarboxylic acid, obtained by the ring-opening of the furfurylidene ketone (b. p. 126°/19 mm.) in alcoholic hydrochloric acid which was considered to be 1-(2-furyl)-1-penten-3-one in the previous papers[6].

8) R. Willstätter and C. H. Clarke: *Ber.*, **47**, 298 (1914).

Summary

3-Acetyl-4-(2-furyl)-3-buten-2-one (I) and ethyl α-propionyl-2-furanacrylate (V) were obtained by the condensations of furfural with acetylacetone and ethyl propionylacetate by piperidine, respectively.

3-Acetyl-4-(2-furyl)-3-buten-2-one (I) was oxidised by sodium hypochlorite to furfurylidenemalonic acid (II), and, on refluxing with alcohoric hydrochloric acid and subsequent hydrolysis, gave β-(4-acetyl-5-methyl-2-furyl)-propionic acid (IV).

Ethyl α-propionyl-2-furanacrylate (V) gave γ,ζ-dioxopelargonic acid (VI) by refluxing with alcoholic hydrochloric acid and subsequent hydrolysis.

The dioxocaboxylic acid (m. p. 83~84°), obtained by the ring-opening of the furfurylidene ketone (b. p. 126°/19 mm.) in alcoholic hydrochloric acid which was considered to be 1-(2-furyl)-1-penten-3-one (VII) in the previous reports, was identical with this γ,ζ-dioxopelargonic acid (VI). It was confirmed, therefore, that the ideas in the previous reports[6] was correct.

The author expresses his sincere thanks to Dr. T. Hayashi for his kind advice.

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The Effect of Conversion on the Mechanism of Vinyl Polymerization. I. Styrene

By Saburo FUJII

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Introduction

Although the detailed mechanism of the initial stage of vinyl polymerization has been studied by many workers with various methods, little has been published which clarifies the effect of conversion on the chain mechanism of polymerization. As already reported, the polymerizations of several vinyl monomers in the liquid phase are strongly accelerated after certain conversions[1),2),3)], and this rate of acceleration has been attributed by Trommsdorff[4)] to a decrease in the termination rate constant of polymer radicals with the increasing viscosity of the system. His suggestion has recently been confirmed by Matheson and his coworkers[5)] with the measurement of the lifetime of kinetic chains, but the further investigations at high conversions may yet be necessary to make clear the chain mechanism in the later stage of polymerization.

In an attempt to obtain further information on this point the present author has studied photochemically the polymerizations of several vinyl monomers in the range 0 to about 70% conversion. This paper reports the work on styrene.

Theoretical

The following facts are implicitly assumed in this work (1) The radical polymerization consists of four kinds of elementary reactions; thermal or light initiation, propagation, transfer with monomer and termination. (2) These elementary rate constants are independent of the length[6)] or valence character (mono- or di-radical) of the polymer radicals, and further the rate constants of propagation and transfer are assumed to be approximately independent of conversion[7)]. (3) The irradiated light is absorbed uniformly in the reaction cell and causes no decomposition of the monomer or of the polymer. (4) The rate of light initiation is proportional to the absorbed light intensity, this intensity being proportional to that of illumination. (5) The light absorption by the polymer is negligible compared to that by the monomer. (6) An instantaneous steady state is reached in the light initiation. (7) The rate of thermal initiation is unaffected by light. (8) The assumptions in the sector experiment are almost the same as those described in Matheson's papers[5)]; precautions to insure the correctness of the assumptions (3) to (8) except (6) were made in the present experiment.

On the basis of the absorption spectra of styrene and its polymer[8)], the assumptions (4) and (5) may be adequate and the absorbed light intensity, I_{abs}, will be represented by

$$I_{abs} = \varepsilon l[M] I_0 , \qquad (1)$$

where I_0 is the intensity of illumination, $[M]$ the monomer concentration, l the depth of the reaction cell and ε the mean molecular extinction coefficient of the monomer in the neighborhood of 3660 Å. In the present work, the production and disappearance of kinetic chains are mainly discussed, but neither the question whether the active polymer is monoradical or biradical or whether the termination is a recombination or a disproportionation are considered. From this stand-point by the concentration of kinetic chains, $[R]$, will be given by

$$\frac{d[R]}{dt} = qI_{abs} + k_i[M]^2 - k_t[R]^2 \qquad (2)$$

and also the rate of monomer consumption at any stage by

$$-\frac{d[M]}{dt} = V_p = k_p[R][M] \qquad (3)$$

Here q is the quantum efficiency of production of kinetic chains, and k_t, k_p and k_i are the rate constants of termination, propagation and thermal initiation respectively.

1) G. V. Schulz and F. Blaschke, *Z. physik. Chemie*, **B50**, 305 (1941).
2) G. M. Burnett and H. W. Melville, *Nature*, **153**, 661 (1945); *Proc. Roy. Soc. London*, **A189**, 456 (1947).
3) M. H. Mackay and H. W. Melville, *Trans. Faraday Soc.* **45**, 323 (1949).
4) Trommsdorff, "*Colloquium on High Polymers*" Freiburg, 1944.
5) (a) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *J. Am. Chem. Soc.*, **71**, 497 (1949); (b) ibid., **73**, 1700 (1951) (c) ibid., **73**, 5395 (1951).
6) F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 3689 (1948); R. A. Cregg and F. R. Mayo, ibid., **70**, 2373 (1948).
7) M. F. Vaughan, *Trans. Faraday Soc.*, **48**, 576 (1952).
8) (a) T. G. Majury and H. W. Melville, *Proc. Roy. Soc. London*, **A205**, 496 (1951); (b) J. H. de Boer, R. Houwink and J. F. H. Custers, *Rec. trav. Chim.*, **52**, 709 (1933).

Further if the condition, $q I_{abs} \gg k_i[M]^2$, is held in the stationary state of this chain reaction, the following two equations are easily derived from eqns. (1), (2) and (3).

$$\ln V_{pL} = \ln\left\{(q\varepsilon l)^{1/n}\frac{k_p}{k_t^{1/n}}[M]^{1+\frac{1}{n}}\right\} + \frac{1}{n}\ln I_a \tag{4}$$

and

$$E_a = -R\frac{\partial(\ln V_{pL})}{\partial(1/T)} = E_p - \frac{1}{n}\left\{E_t + R\frac{\partial(\ln q)}{\partial(1/T)}\right\} \tag{5}$$

where V_{pL} is the stationary rate of photo-polymerization, E_a the over-all activation energy of photo-polymerization, T the absolute temperature, and E_p and E_t are the activation energies of propagation and termination respectively. These eqns. (4) and (5) will be used in the discussion of the experimental results.

Next, if the chain termination is of the second order ($n=2$), the average life-time of kinetic chains, τ_s, in the stationary state of polymerization may be defined by

$$\tau_s = \frac{1}{k_t[R]_s} \tag{6}$$

and then

$$\frac{\tau_s V_{pL}}{[M]} = k_p/k_t \tag{7}$$

is obtained from eqn. (3). Thus, by measuring τ_s the value of k_p/k_t can be estimated.

Under the present experimental conditions the value of τ_s at low conversion (0~1%) was of the order of second and could be measured with rotating sector technique, but the one at high conversions became so long (over 10^3 seconds) that the photochemical after-effect could easily be observed dilatometrically. For the after-effect the equation governing $[R]$ after the interruption of illumination will be

$$-\frac{d[R]}{dt} = k_t[R]^n - k_i[M]^2 \tag{8}$$

This equation can be integrated in the case of $n=2$ under the conditions ($[R]=[R]_s$ at $t=0$, $[R]=(k_i/k_t)^{1/2}[M]=[R]_d$ at $t=\infty$) and combined with eqns. (3) and (6) to give

$$\ln\left(\frac{V_p+V_d}{V_p-V_d}\right) = \ln\left(\frac{V_{pL}+V_d}{V_{pL}-V_d}\right) + 2\frac{V_d}{V_{pL}}\frac{t}{\tau_s} \tag{9}$$

where V_d is the steady rate of thermal polymerization (dark rate) V_p the rate of polymerization at the time, t, after the interruption of illumination. Hence if

$$\left[\frac{V_{pL}}{2V_d}\ln\left(\frac{V_p+V_d}{V_p-V_d}\right)\right]$$

is plotted as a function of t, a straight line will be obtained with a slope of $1/\tau_s$, that is, τ_s can be estimated.

The theory and experimental method of the rotating sector are fully presented in Matheson's papers[5]. In the present experiment the ratio of the dark period to the light period was 3 and the thermal initiation during light periods was negligible compared to the light initiation. Therefore the theoretical ratio of the intermittent light rate to the steady light rate as a function of flash time and dark rate is the same as the one calculated by Matheson and his co-workers.[5a]

Experimental

Styrene was prepared by the dehydration of pure β-phenyl-ethyl alcohol with solid potassium hydroxide over 240°C. and purified by successive washing with dilute sulphuric acid, dilute sodium hydroxide and distilled water. After drying with calcium chloride it was distilled twice through a fractionating column of 1 meter long at 15 mm. pressure, and the fraction boiling at 40.0°C. was collected and stored in an evacuated flask in the dark. Immediately before use this monomer was allowed to polymerize to about 5% thermally and with the illumination of ultra-violet light longer than 3300 Å, and then it was redistilled with dry ice into the reaction cell. These procedures were carried out in a glass system evacuated to 10^{-3}mm. pressure.

The rate of monomer consumption was measured with a dilatometer shown in Fig. 1, and a reading-microscope was used to read the mercury level in the capillary C to 0.01 mm. This dilatometer was immersed in a thermostat, which was regulated to ±0.001°C. In the experiments at high conversions the reaction cell A in Fig. 1. was heated in a small electric furnace at 130±5°C. for desirable duration[9], left alone at room

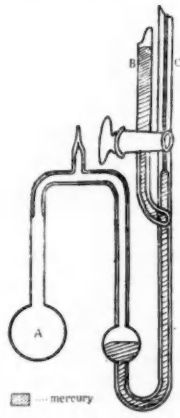

Fig. 1. Dilatometer

9) The number average degree of polymerization for the polymer formed by this procedure may be estimated as about 1700 (R. A. Gregg and F. R. Mayo, *Discussions of the Faraday Soc.*, No. 2 (1947). *The Labile Molecule*. p. 328.)

temperature over half a day, and then the experiments were carried out, where the polymer concentration in A was estimated from the lowering of the mercury level in B. Matheson's data[5b] about the densities of the monomer and of the polymer in monomer were used to estimate the rate of polymerization and the polymer concentration in the cell.

The source of light was a 200 watt ultra high pressure mercury lamp fed from a constant voltage transformer. The light was passed through a 5% aqueous solution of copper sulphate and through two lenses made of soda glass. Considering the intensity distribution of absorbed light the photo-polymerization may be mainly caused by the light of 3660 Å.[10] During an experiment the constancy of light was checked by a vacuum photocell with a Mazda UVD_1 filter (for 3660 Å). Also, using the above optical filter, the light intensity at the front of the reaction cell was measured with an uranyl-oxalate actinometer and its full intensity was 4×10^{-8} Einsteins per second.

The sector was made of a 46 cm. diameter aluminum disk and one-fourth part of it was cut off to a radical depth of 7 cm. The disk speed could be varied in steps from 1/20 to 150 r. p. m. The set of sector apparatus and the method of sector experiment were almost the same as the ones reported by Matheson and his co-workers.[5a]

Unless otherwise noticed, the reaction system did not contain any photo-sensitizer or thermal catalyser. The rate of photo-polymerization under the present experimental conditions did not exceed over 10^{-4} mol./l./sec., so that the apparent change of monomer concentration may be negligible during illumination. When the lifetime of kinetic chains was very long, a long period o preliminary illumination was necessary to the determination of the stationary rate of photo-polymerization.

Results

The stationary rates of photo-polymerization under a constant light intensity (4×10^{-8} Einsteins/sec.) and of thermal polymerization were measured at three different temperatures between 0 to 60 % conversion, and these were found to be strongly accelerated with increasing conversion (Table I). Plotting log (relative rate) against the reciprocal of the absolute temperature gives an over-all activation energy at each conversion and the result is indicated in the last column of Table I.

TABLE I

RATES* OF PHOTO- AND THERMAL-POLYMERIZATIONS AND OVER-ALL ACTIVATION ENERGIES FOR STYRENE

Conversion %	25°C.	30°C.	40°C.	$E_{act.}$ (k cal./mol.)
(a) Light rate (unit; 10^{-6}mol./l./sec.)				
0~1	1.15	1.52	2.65	10.4
38±1	6.25	7.91	12.0	8.1
60±2	21.3	25.8	37.2	6.9
(b) Thermal rate (unit; 10^{-6}mol./l./sec.)				
0~1	0.097	0.170	0.417	18.1
38±1	0.396	0.630	1.40	15.7
60±2	0.645	1.01	2.17	14.5

* All the rate measurements were corrected for the thermal reaction taking place in the unilluminated appendages to the reaction cell, by subtracting the proper fraction of thermal rate from the apparently observed rates. The polymer concentration in the unilluminated appendages to the cell did not exceed a few per-cent even after the experiments at high conversions, so that the magnitude of the thermal rate in that part, which was necessary to the above correction, was considered to hold the initial value in a complete run.

In this experiment the rate acceleration was found to be accompanied with the photochemical inital- and after-effects (Fig. 2) and also with by a decrease in the reaction order of chain termination (Table II). Here Fig. 2 was obtained in the direct observation of the volume change with time of the reaction system after the interruption of light, where these results had been confirmed to be mainly caused by the chemical after-effect but not by the temperature depression of the system. In the low rate of polymerization

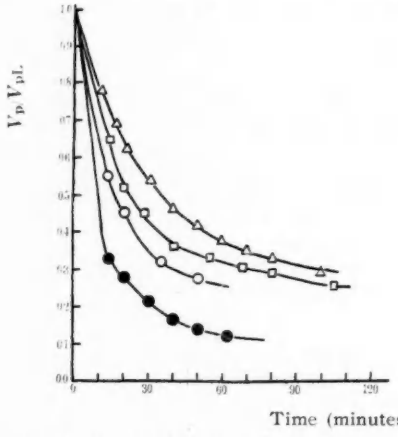

Fig. 2. Photochemical after-effects at 30°C.

	Conversion %	V_{pL} mol./l./sec.	V_d/V_{pL}
●	38	7.91×10^{-6}	0.081
○	38	3.58×10^{-6}	0.180
□	43	9.32×10^{-6}	0.054
△	60	25.8×10^{-6}	0.038

used in these experiments (of the order of 10^{-5} mol./l./sec.) the temperature within the reaction cell exceeded that of the thermostat

10) G. M. Burnett, *Trans. Faraday Soc.*, **46**, 772 (1950).

bath only by the order of 0.01°C. under the stationary conditions, and the volume change due to the disappearance of this temperature difference might be negligible, at high conversions, compared to the total change caused by the after-effect. The data in Table II were obtained, with the use of eqn. (4), from the measurement of V_{pL} in one run in the same reaction cell, (i) under the full intensity from the lamp and (ii) with the intensity reduced by covering the window with calibrated screens.

TABLE II
REACTION ORDER OF CHAIN TERMINATION AT 25°C.

(a) An example at 68 % conversion

Transmission of screen, S	V_{pL} (10^{-5} mol./l./sec.)	$\log S$	log (Relative rate	n
1.00	2.25	0.00	0.00	
0.41	1.24	−0.38	−0.25	1.5
0.19	0.79	−0.73	−0.45	1.6

(b) Summarized result

conversion, %	n
0	1.9～2.1
38±1	1.9～2.1
60±2	1.7～1.8
68±2	1.4～1.6

Also the lifetime of kinetic chains was measured or estimated at several conversions in order to obtain the relationship between the above results and the relative change of k_t with increasing conversion. Since the overall rate of photo-polymerization in the initial stage was proportional to the square-root of the absorbed light intensity ($n=2$, as shown in Table II) and was constant during a considerable period of illumination, τ_s at extremely low conversions could be measured with rotating sector. A typical run in the sector experiments is indicated in Fig. 3.

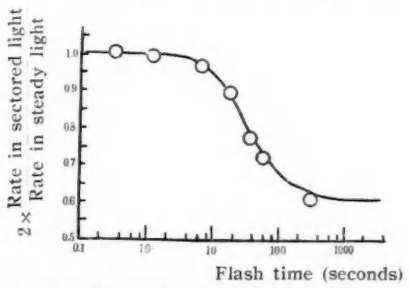

Fig. 3. Rates of polymerization in intermittent light for different times of flash: Curve, theory for dark rate 7 % of steady light rate; ○, experimental point under the conditions (temp. 30°C., coversion 0 % and steady light rate $=2.27\times10^{-6}$ mol./l./sec.)

On the other hand the values of τ_s at high conversions were too great to be measured by with the usual sector technique and so these were estimated by the use of eqn. (9) from the observed after-effect. The allowance for the deviation of n from 2 was not considered in this estimation. Therefore both the τ_s values estimated on the basis of the eqn. (9) and the corresponding k_p/k_t values on the eqn. (7) may have a considerable error at the conversions over about 60 %, since n becomes less than 2 at those high conversions. Few examples of the analytical representation for the after-effect observed are illustrated in Fig. 4 and the results of all lifetime runs are summerized in Table III.

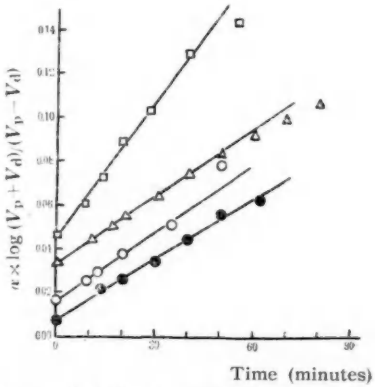

Fig. 4. Analytical representations for the observed after effects; the kinds of experimental points are the same as the ones shown in Fig. 2.

●, ○ ····· $\alpha=0.1$
□, △ ····· $\alpha=1.0$

Discussions

Rate acceleration Trommsdorff[4] examined several vinyl monomers and found that the rates of polymerization were accelerated after certain conversions, styrene alone showing no such acceleration under his experimental conditions. Also it has been well known after Schulz's work[11] that the rates of thermal polymerization of styrene at comparatively high temperatures are apparently proportional to the monomer concentration in the range up to about 90 % conversion. Therefore, compared with these previous results, the abnormal rate acceleration observed in this work seems to throw the possibility (a) on the production of an unstable substance which may induce the rate acceleration and the after-effect or (b)

11) G. V. Schulz, *Ergeb. d. exakt. naturwis.*, **17**, 364 (1938).

TABLE III KINETIC CHAIN LIFETIMES AND RATE CONSTANT RATIO IN RTYRENE

Conversion x %	Temp., °C.	V_{pL} mol./l./sec.	τ_s sec.	Av. τ_s at $V_{pL}=10^{-5}$	k_p/k_t	k_{tx}/k_{to}(b)
0	20	2.18×10^{-5}	0.26	0.48	0.55×10^{-3} (a)	
		1.12×10^{-5}	0.35			
	30	2.27×10^{-5}	9.8	2.0	2.36×10^{-3}	1
		1.52×10^{-5}	12.			
38±1	30	7.91×10^{-5}	453.	358.	6.36×10^{-4}	3.75×10^{-2}
		3.58×10^{-5}	1000.			
43±2	30	9.32×10^{-5}	1356.	1261.	2.56×10^{-3}	9.22×10^{-4}
60±2	30	2.58×10^{-5}	1932.	4980.	1.30×10^{-2}	1.81×10^{-4}
70±2	30	1.76×10^{-5}	2274.	4002.	1.37×10^{-2}	1.71×10^{-4}

(a) α-Azo-bisisobutyronitrile was used as a photo-sensitizer in this experiment, no sensitizer in the others.

(b) The ratio of k_{tx} at x % conversion to k_{t0} at nearly 0 %; the assumption (2) was used in this estimation.

on the abnormal increase of q. However the theoretical examination for the case (a) will give a constant τ_s value, which is independent of V_{pL} and conversion, in contradiction to the present result, and also the simple calculation for the case (b) will lead to the unreal conclusion that the few hundred-fold increase of q must be necessary to explain the observed rate acceleration. On the other hand, if the rate acceleration is attributed to a decrease in k_t as suggested by Trommsdorff in the other vinyl polymerizations, the expected ratios of V_{pL} at 38 % and 60 % conversions to the initial value may eb estimated as about 7.9 and 18.8 respectively at 30°C. by the use of eqn. (4) with the data in the last column of Table III, while the corresponding experimental ratios are about 5.2 and 16.9 respectively. The difference between the above two values at each conversion is accepted to be within an experimental error under the present conditions. Thus the allowance for the above discussions will lead to the conclusion that the rate acceleration is due to an extreme decrease in k_t as the system becomes more viscous.

Decreases in the overall activation energy and n It is an expected result in this work that an extreme decrease in k_t is accompanied with a considerable decrease in the over-all activation energy, and this kinetic behaviour has also been found by the present author in the thermal- and photo-polymerizations of methyl methacrylate near room temperatures[12] and by Cowley & Melville[13] in the photo-degradation (by 2537 Å line) of polymethyl methacrylate over 130°C. This result can be explained by the fact that E_t in eqn. (5) increases steadily as the mutual termination of polymer radicals become diffusion-controlled with the increasing viscosity of the system. Using the following equation, which has been suggested by Spencer and Williams[14],

$$\eta = 3.63\times10^{-10}\, exp\,\{0.0572\sqrt{M} + \sqrt{w_2}\,(22.54 - 0.045\sqrt{M} + 5000/T)\},$$

where η=bulk viscosity of the styrene-polystrene system in centipoises, M=Staudinger molecular weight and w_2=weight fraction of polymer, it may be estimated that the activation energies of diffusion of polymer radicals at 38 % and 60 % conversions are about 6.1 and 7.7 kcal./mole respectively. If 2.4 kcal./mole is used as an apparent E_t value in the initial stage[5b], the estimated increase in E_t will cause it to decrease E_a (in eqn. (5)) by about 1.8 kcal./mole at 38 % and by about 3.0 kcal./mole at 60 %, while Table I shows the decreases in the over-all activation energies as 2.3~2.4 kcal./mole at 38 % and as 3.5~3.6 kcal./mole at 60 %. The difference between the above estimated and experimental decreases in E_a may be within an experimental error.

The value (1.9~2.1) of n, the reaction order of chain termination, measured in the range 0 to nearly 40 % conversion shows that mutual termination only takes place. However its decrease over about 60 % conversion suggests strongly that self-termination occurs considerably in the highly viscous medium. It is not difficult to visualize a mechanism by which polymer radicals become apparently terminated without mutual collision. There will be a finite probability that the active end of a growing radical will become shielded by the coiling of the molecule. The fine net of polymer chains at high conversion would be expected greatly to enhance the

12) Unpublished work from this Laboratory.

13) P. R. E. J. Cowley and H. W. Melville, *Proc. Roy. Soc. London*, **A211**, 320 (1952).

14) Spencer and Williams, *J. Colloid Sci.*, **2**, 117 (1947).

degree of shielding. Thus a considerable portion of radicals become unable to react freely with monomer for steric reasons and appear to be deactivated by itself alone. In this sense the extreme decrease in k_t is an inevitable result and also the rate constants of propagation and transfer may be more or less reduced at very high conversions. On the other hand such a shielding effect may be expected to be diminished by the following factors; (i) thermal disturbance, (ii) a decrease in the molecular weight of polymer present and (iii) the addition of a chain transfer substance which is able to pass freely through the polymer network. The factor (iii) has been confirmed experimentally by the addition of a small amount of carbon tetrachloride as a chain transfer substance in the photo-polymerization of styrene[15]. Also it is expected from the factor (i) that neither the extreme decrease in k_t nor the change of n are observed at comparatively high temperatures. The discrepancy between the present experimental results and those of the previous authors may perhaps be due to a great difference in the degree of this shielding effect, though it can not be explained precisely at present.

Summary

The polymerization of pure styrene has been studied photochemically near room temperatures and in the range 0 to about 70% conversion, and the following results have been obtained.

With increasing conversion; (1) both the direct photo-polymerization and the thermal polymerization are accelerated strongly, (2) the over-all activation energies in both polymerizations decreases, (3) the lifetime of kinetic chains increased steadily and the photochemical initial and after effects are easily observed dilatometrically over 30% conversion. Also (4) the reaction order of chain termination is 2 in the range 0 to about 40% conversion, but it becomes less than 2 at the conversions over 60%.

Thus these results have been discussed on several assumptions and it has been concluded that they are attributed to a considerable change in the mechanism of radical termination with increasing conversion of the reaction system, i.e., the change from an activation-controlled termination to a diffusion-controlled one.

The author wishes to express his hearty thanks to Dr. Shoji Shida of this Institute for his helpful advice and encouragement, and to Dr. Hideya Funahasi to Takasago Perfumery Co. for his kind gift of β-phenylethyl alcohol.

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15) Unpublished work by the present author.

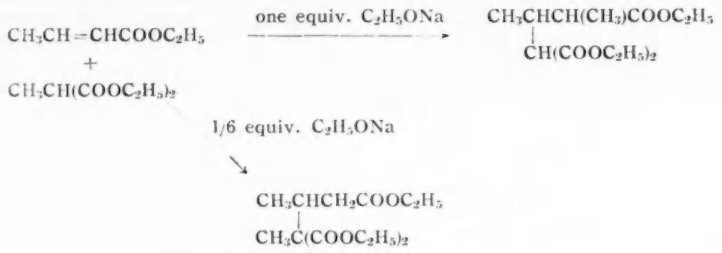
The Michael Addition of Diethyl Methylmalonate to Ethyl Crotonate-(carbonyl C^{14}). A Contribution to the Elucidation of the Mechanism of the Abnormal Addition

By Osamu SIMAMURA, Naoki INAMOTO and Tadashi SUEHIRO

(Received March 15, 1954)

In the course of a paper on the constitution of ethyl sodiocyanacetate and of ethyl sodiomethylcyanacetate, Thorpe[1] has put forth a view that these sodio compounds, $RC(CN):C(ONa)OC_2H_5$ (R=H or alkyl), add to the double bond of α,β-unsaturated carboxylic esters with R- and $-C(CN):C(ONa)OC_2H_5$ acting as addendum components. More recently, Michael and Ross[2] have shown that diethyl methylmalonate in the presence of one sixth equivalent of sodium ethoxide adds to ethyl crotonate to yield diethyl α-ethoxycarbonyl-α,β-dimethylglutarate, whereas, with one equivalent of sodium ethoxide, the product is diethyl α-ethoxycarbonyl-β,γ-dimethylglutarate in accordance with Thorpe's view. A product of the former type in the Michael addition is often referred to as normal by later workers and one of the latter type as abnormal.

1) J. F. Thorpe, *J. Chem. Soc.*, **77**, 923 (1900).
2) A. Michael and J. Ross, *J. Am. Chem. Soc.*, **52**, 4598 (1930).



It has then been suggested by Holden and Lapworth[3] that the abnormal addition product with a structure expected from Thorpe's theory could result equally well by migration, during the addition process, of an ethoxycarbonyl group from the malonic ester part of the adduct; however, they were unable to produce any convincing experimental evidence in favour of the theory. Gardner and Rydon[4] have subsequently shown that all the then available observations can be accounted for on the basis of the Holden-Lapworth mechanism; but it has been viewed with some suspicion because of the strained four-membered cyclic structure postulated as an intermediate. It has now been definitely established by a tracer method with carbon-14 that, in the Michael addition of diethyl methylmalonate to ethyl crotonate with one equivalent of sodium ethoxide, it is an ethoxycarbonyl group which migrates to yield the abnormal addition product.

Labelled ethyl crotonate was condensed with diethyl sodiomethylmalonate, and the resulting diethyl α-ethoxycarbonyl-β,γ-dimethylglutarate hydrolyzed with sodium hydroxide to the corresponding tricarboxylic acid, which was subsequently decarboxylated by heating at 170–180°. The carbon dioxide evolved was found to contain about 42 % of the radioactive carbon of the original ethyl crotonate. This observation demonstrated beyond doubt that in the course of the condensation migration of an ethoxycarbonyl group took place from the methylmalonate moiety to the carbon atom α to the labelled ethoxycarbonyl group giving a product (II) with a malonic ester grouping labelled with C^{14}. If a methyl group had become attached to the carbon atom α to the labelled ethoxycarbonyl group as postulated by Thorpe[1] and Michael and Ross[2], the resulting condensation product could have contained no labelled malonic ester grouping, and the subsequent hydrolysis followed by pyrolysis could have consequently given no radioactive carbon dioxide. The sequence of the reactions followed is shown as follows and the measured activities of the products at each stage of the reactions given in Table I.

3) N. E. Holden and A. Lapworth, *J. Chem. Soc.*, **1931**, 2368.
4) J. A. Gardner and H. N. Rydon, ibid., **1938**, 48.

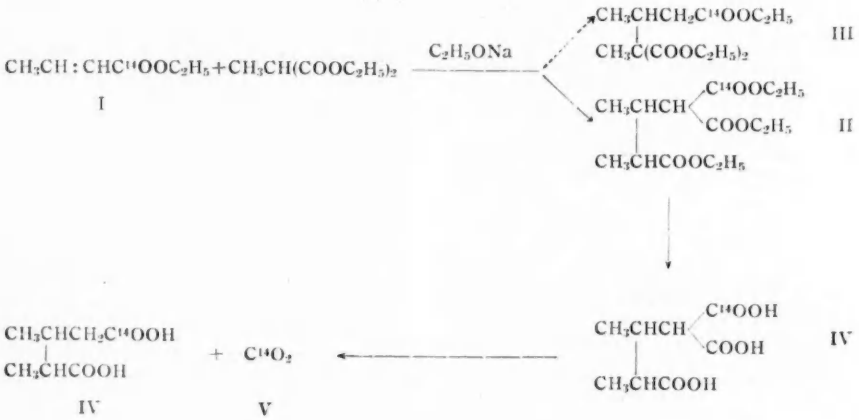


TABLE I

MOLAR ACTIVITIES* OF THE REACTION PRODUCTS

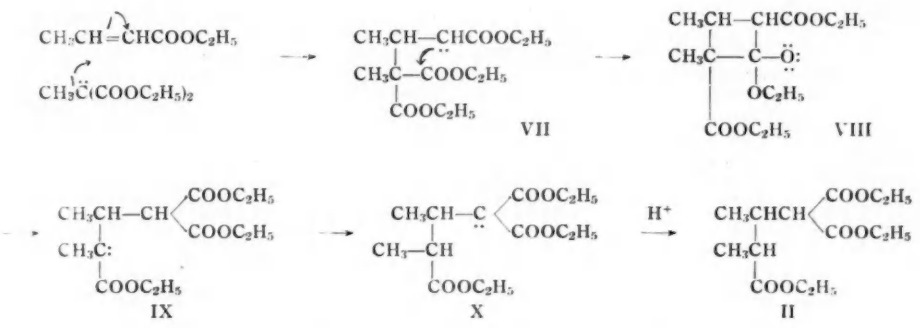
	Expt. 1 mc./mol.	Expt. 2 mc./mol.
Ethyl crotonate (I)	0.0805±0.0013	0.0285±0.0006
Diethyl α-ethoxycarbonyl-β,γ-dimethylglutarate (II)	0.123 ±0.003	0.0415±0.0018
α-Carboxy-β,γ-dimethylglutaric acid (IV)	0.120 ±0.003	0.0399±0.0013
Carbon dioxide from decarboxylation (V)	0.0335±0.0007	0.0120±0.0004
Carbon dioxide from combustion of the residue (VI)	—	0.0043±0.0002

* Indicated deviations are standard errors.

In the course of the investigation some difficulty arose with regard to some molar activity values. Molar activities of diethyl α-ethoxycarbonyl-β,γ-dimethylglutarate (II) and the corresponding free tricarboxylic acid were unusually high compared with the theoretical values of 0.0805 and 0.0285 expected from the activities of the starting materials. This anomaly is probably attributable to the contamination with labelled diethyl α-ethylidene-β-methylglutarate, which may have been formed by the dimerization of the labelled ethyl crotonate in the presence of basic reagents[5]. It seems that the fractionation was not carried out effectively owing to the smallness of the quantity of the material to be handled. On the basis of the measured molar activities, the contents of the dimer of ethyl crotonate in the condensation products are calculated to be 49 and 39 mole% for Expts. 1 and 2, respectively. The alkaline hydrolysis of the condensation product did not give crystalline acid; this is due to the presence of diastereomeric forms of the tricarboxylic acid (IV) in addition to the acid from the above dimer. The observed neutralization equivalents of the products (72.7 and 73.9 for Expts. 1 and 2, respectively) were higher than the theoretical value of 68.1 for α-carboxy-β,γ-dimethylglutaric acid; the differences are accounted for quantitatively by correcting for the presence of the crotonic acid dimer. Further, the activity of the carbon dioxide obtained by oxidation of the residue from the decarboxylation was found to be 0.0043 mc./mol., which agrees well with 0.0044 mc./mol. calculated from the composition of the condensation product.

It is generally recognized that the C^{12}-carboxyl group is eliminated as carbon dioxide from malonic and substituted malonic acids several per cent more frequently than the C^{14}-carboxyl group.[6] On the tentative assumption that the difference in the reaction rate is ten par cent, the molar activity of the carbon dioxide evolved from α-carboxy-β,γ-dimethylglutaric acid in, for example, Expt. 2 should be 0.0285/(1.10+1.0)=0.0136 mc./mol. The observed value of 0.0120 mc./mol. appears therefore to be too low. This is probably attributed to the possible presence of a small quantity of the unrearranged normal product (III).

An essential part of the mechanism of the Michael addition with migration of an ethoxycarbonyl group may be formulated as follows:



5) H. v. Pechmann, *Ber.*, **33**, 3323 (1900); A. Michael and J. Ross, *J. Am. Chem. Soc.*, **53**, 1150 (1931).

6) G. A. Ropp, *Nucleonics*, **10**, No. 10, 22 (1952)

The carbonyl oxygen of the migrating ethoxycarbonyl group plays a role in helping the carbonyl carbon to accept a lone pair of electrons from the carbon atom α to the ethoxycarbonyl group on the original ethyl crotonate resulting in a four-membered cyclic structure provisionally shown as VIII. Objection might be raised to such a structure which may suffer from a considerable strain, but the four-membered cyclic compounds are not so strained that their existence should be rendered impossible. It may be considered that structure VIII represents a transitional state of the rearrangement rather than a more or less stable intermediate, the acceptance of the lone pair being synchronized with the release of the electron pair which has originally linked the migrating group with the α carbon atom of the original diethyl methylmalonate, giving rise to IX. The migration of the ethoxycarbonyl group is followed by a transfer of a proton in the reverse direction to it, X thus being formed, in which a carbanion group is more stabilized than in IX. It is possible that the transfer of the proton may be simultaneous with the migration of the ethoxycarbonyl group. This is a natural consequence of the difference in acidity between a CH group activated by one ethoxycarbonyl group and one activated by two such groups, the acidity of the former being less strong than the latter. Finally, X gives the rearranged product (II) on working up with aqueous acid.

If there is, in the reacting mixture, a stronger acid which can donate a proton to a lone pair of electrons shown in structure VII, the migration of an ethoxycarbonyl group will not take place. This is indeed the case with the Michael condensation with one sixth equivalent of sodium ethoxide[2]; diethyl methylmalonate which had not completely been converted to the sodio compound served as a proton donor. Tsuruta, Yasuhara and Furukawa[7] investigated the effect of variation of experimental conditions, specially of the amount of sodium ethoxide in the Michael addition of diethyl ethylmalonate to diethyl fumarate on the relative yield of the normal and abnormal products and pointed out a competition between the reaction of the initially formed adduct anion (similar to VII) with a proton donor giving the normal product and the isomerization of the adduct anion leading to the abnormal product; but the mechanism of the latter reaction was obscure to them.

As regards what types of reactants will show abnormality and what types will be normal, the theory of the abnormal addition discussed above predicts that condensation of unsaturated compounds of the type CR_2: $CHCOOC_2H_5$ with alkylmalonic ester and similar compounds can be abnormal, and that those of unsaturated substances of the type CR_2: $CRCOOC_2H_5$ with malonic esters will be normal.

Experimental

Crotonic Acid-(carboxyl-C^{14}) This acid was synthesized by the carbonation with radioactive carbon dioxide of allymagnesium bromide prepared according to Shoemaker and Boord[8] followed by the isomerization with hot 50% sulfuric acid[9] according to the following scheme.

$$CH_2:CHCH_2MgBr + C^{14}O_2 \longrightarrow CH_2:CHCH_2C^{14}OOH$$

$$CH_2:CHCH_2C^{14}OOH \longrightarrow CH_3CH:CHC^{14}OOH$$

Starting from 393 mg. of active barium carbonate containing 0.12 mc. of C^{14} and diluting the resulting crude labelled crotonic acid with a total of 2.0 g. of pure unlabelled crotonic acid as a carrier for ease of manipulation, 0.48 g. of labelled crotonic acid with constant activity of 0.245 ± 0.0043 mc./mol., m.p. 70.5–72.0°, was obtained after crystallization four times from petroleum ether. On the basis of the molar activity of the crotonic acid the overall yield of the above synthesis is estimated at 4.9% based on the carbon dioxide used. The poor yield is attributed to the carbonation step, as the isomerization appears to be effected with an almost quantitative yield of 98% according to the literature.[9]

Another approach to labelled crotonic acid followed consisted in the action of labelled potassium cyanide on allyl bromide at 100° in a sealed tube, and the subsequent hydrolysis and simultaneous isomerization to crotonic acid by heating the resulting ally cyanide with 50% sulfuric acid on a water bath.

$$CH_2:CHCH_2Br + KC^{14}N \longrightarrow CH_2:CHCH_2C^{14}N$$

$$CH_2:CHCH_2C^{14}N \longrightarrow CH_3CH:CHC^{14}OOH$$

7) T. Tsuruta, Y. Yasuhara and J. Furukawa, *J. Org. Chem.*, **18**, 1246 (1953).
8) B. H. Shoemaker and C. E. Boord, *J. Am. Chem. Soc.*, **53**, 1505 (1931).
9) E. J. Boorman and R. P. Linstead, *J. Chem. Soc.*, **1933**, 577.

This method gave an overall yield of 25% based on the cyanide used.

Ethyl Crotonate-(carbonyl-C^{14}) The synthetic procedure was similar to that for ethyl acetate by Ropp.[10] Crotonic acid-(carboxyl-C^{14}) (1.1 g.) was neutralized with aqueous sodium hydroxide, the resulting solution evaporated to dryness on a water bath, and the remaining labelled sodium crotonate desiccated at 120° under 5×10^{-4} mm.Hg. This was heated for one hour at 180–210° with 3.8 cc. of ethyl phosphate, b.p. 104–5° at 20 mm. Hg, prepared according to the method of Dutton and Noller.[11] Distillation of the reaction mixture at 2×10^{-4} mm. Hg gave 1.3 g. of ethyl crotonate-(carbonyl-C^{14}). This procedure yielded pure specimen of ethyl crotonate, n_D^{20}1.4247, in a preliminary experiment with unlabelled crotonic acid.

The Michael Addition Two similar runs were carried out, one of which (Expt. 2) is described as an example. Sodium (0.5 g.) was melted by heating in xylene and powdered by shaking, the xylene decanted, the sodium washed with ether, and 100 cc. of ether and 1.3 g. of absolute ethyl alcohol added to prepare sodium ethoxide. To this mixture 3.8 g. of diethyl methylmalonate prepared from methyl iodide and diethylsodiomalonate in alcohol according to the usual practice, b.p. 114.0–114.5° at 46 mm Hg, was added. Ethyl crotonate-(carbonyl-C^{14}) (2.21 g., 0.0285 mc./mol.) in 50 cc. of ether was then added dropwise to the stirred mixture and the mixture was refluxed for 5 hours. Acetic acid (1.6 g.) in 12.5 cc. of water was added with stirring, the ethereal layer separated, dried with anhydrous sodium sulfate, the ether removed on a water bath and the residue subjected to distillation under diminished pressure, giving 1.7 g. of a fraction (II) boiling at 130–131° at 3 mm. Hg. The condensation product was heated with 1.0 g. of sodium hydroxide in a mixture of 5 cc. each of water and alcohol for two hours and a half on a water bath, the alcohol removed, the residue diluted with water to 80 cc. and filtered through a column of Amberlite IR 120. A fraction with *p*H 2.2 was collected and evaporated to dryness over sulfuric acid in a vacuum desiccator, giving 1.1 g. of acid (IV) (neutralization equivalent, 73.9; activity, 0.0399± 0.0013 mc./mol.).

Decarboxylation of α-Carboxy-β,γ-dimethylglutaric Acid The above acid (170 mg.) was heated gradually to 180° in an evacuated vessel, and the vessel was kept at that temperature for one hour. The carbon dioxide evolved was condensed in a trap cooled with liquid air attached to the reaction vessel. When the decarboxylation was over, the condensed carbon dioxide was transferred, also in vacuum, to aqueous sodium hydroxide contained in another flask. Ammonium chloride was added to the sodium hydroxide solution, barium carbonate precipitated by adding barium chloride solution, collected on a filter paper and assayed for radioactivity (Found: 0.0120 ±0.0004 mc./mol.). The same result was obtained, if the decarboxylation and absorption of carbon dioxide by aqueous sodium hydroxide was carried out in an apparatus for Van Slyke-Folch oxidation[12], thus eliminating the operation of condensing carbon dioxide by liquid air.

Radioactivity Determinations Radiocarbon assays were carried out by oxidizing samples according to Van Slyke and Folch[13], and converting the resulting carbon dioxide to barium carbonate, which was counted with a Geiger-Müller counter on an "infinitely thick" layer with a surface area of 4.9 cm^2, the counts being all corrected for background and compared with the count of a standard barium carbonate with known molar activity.

Summary

The Michael addition of diethyl methylmalonate to ethyl crotonate-(carbonyl-C^{14}) was carried out with one equivalent of sodium ethoxide; the addition product, diethyl α-ethoxycarbonyl-β,γ-dimethylglutarate, was hydrolyzed and the resulting acid decarboxylated by heating. The evolved carbon dioxide contained 42% of the radiocarbon of the original ethyl crotonate. Thus it was demonstrated that the migration of an ethoxycarbonyl group took place in the course of the reaction from the methylmalonate moiety to the carbon atom α to the labelled ethoxycarbonyl group. The mechaism of the reaction is discussed.

The authors are indebted to the Ministry of Education for a Grant-in-Aid for Scientific Research.

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10) G. A. Ropp, *J. Am. Chem. Soc.*, **72**, 2299 (1950).
11) R. G. Dutton and C. R. Noller, "Organic Syntheses," **16**, 9 (1936).
12) M. Calvin et al., "Isotopic Carbon", John Wiley & Sons, Inc., New York, 1949, p. 93.
13) D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, **136**, 509 (1940).

An Equation of State in Analytical Form (Continued)

By Tetsuya ISHIKAWA

(Received December 21, 1953)

From the successive studies on this subject[1], the author is convinced that his equation of state is, among the hitherto pubished equations of state, the only one which has applicability to liquids as well as to vapours. As a supplementary example, it is necessary to add a comparison between his equation and Beattie-Bridgeman's equation, the latter having generally been accepted to hold with high accuracy for vapours. Fig. 1 shows a

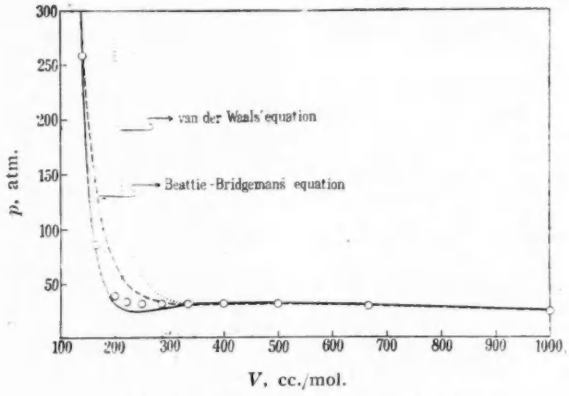

Fig. 1. Critical Isotherm of $C(CH_3)_4$

graphical comparison between these two equations by quoting gaseous neopentane, $C(CH_3)_4$, at the critical isotherm from Beattie, Douslin, and Levine's recent measurements[2] (the author's equation, full line; Beattie-Bridgeman's equation, broken line; observed values, ○). Their calculated values above 3.5 mole/l were not given, and they were computed by use of their determined constants: $A_0=23.3300$, $B_0=0.33560$, $a=0.15174$, $b=0.13358$, $c=400\times10^4$. For the author's curve $(2-\epsilon)$ the value at the critical isotherm was taken to be 1.922, the mean of the values: 1.913, 1.914, 1.917, 1.920, 1.924, 1.927, 1.928, 1.928, 1.927, and 1.926 at 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 and 6.0 mole/l respectively.

As seen from the figure in which van der Waals' equation is also shown by a dotted line, Beattie-Bridgeman's equation behaves like, but far better than, van der Waals' equation as reported in the latest paper. Similar facts are found for a certain range above the critical temperature and also in the case of normal pentane, whose data are quoted from the measurements of the same investigators[3], hence it appears that Beattie-Bridgeman's equation fails at pressures so high as to correspond to the liquid portion in the neighbourhood of the critical temperature. On the other hand, the author's equation, which is valid even at such high pressures as stated above, displays a signoidal curve (showing a maximum and minimum) still above the critical temperature, the reason being easily understood from its derivation from van der Waals' equation. In fact, such a signoidal curve occurs even at a temperature from a few (e.g. H_2) to a few tens degrees (e.g. CO_2, $C(CH_3)_4$, C_2H_4[4]) above the critical temperature, though its supersaturated vapour portion, including the maximum, nearly coincides with the observed values. The necessity of this discrepancy in analytical meaning will be elucidated hereafter.

Phillips[5] carried out interesting experiments on the viscosity of carbon dioxide under a wide range of pressures both above and below the critical temperature. His observed

1) T. Ishikawa, This Bulletin, **26**, 78, 530 (1953); T. Ishikawa, M. Ikeda, ibid., **26**, 516 (1953).
2) J. A. Beattie, D. R. Douslin, S. W. Levine, *J. Chem. Phys.*, **20**, 1619 (1952).
3) J. A. Beattie, S. W. Levine, D. R. Douslin; *J. Am. Chem. Soc.*, **74**, 4778 (1952).
4) Adopted from "International Critical Tables", III, p. 15.
5) P. Phillips, *Proc. Roy. Soc., London*, A**87**, 48 (1912).

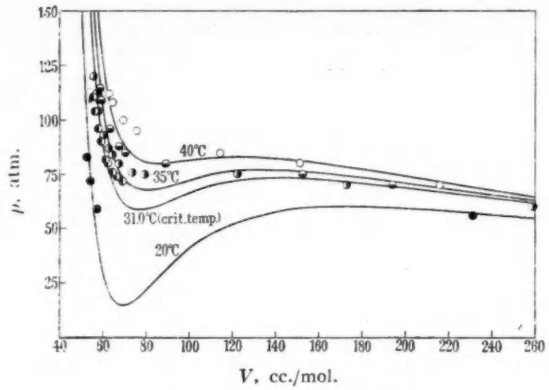

Fig. 2. Isotherms of CO_2

$p-V$ values at and above the critical temperature (denoted by ●, ◐, ◑, ◒, and ○ at 20, 30, 32, 35, and 40°C respectively in Fig. 2) lie fairly close to each isotherm except that which, if vapour and liquid still coexist, corresponds to the superheated liquid portion and the never realizable portion, $(\partial V/\partial p)>0$, of plots of the author's equation (full line), in which $(2-\varepsilon)$ values are computed from the previously obtained linearity, $2-\varepsilon=1.912+0.00028\ (T-T_c)$, except the value, 1.903 at 20°C, which is determined directly from Phillips' data for the reason that the availability of the linearity for vapour state down to a temperature below the critical temperature is at present questionable.

TABLE I

Tests for constancy of H (V-b) and of $H\,V^{2-\varepsilon}$ (H, poise; V, cc./mol.)

20°C			30°C			32°C		
p	H (V-b)	$H\,V^{2-\varepsilon}$	p	H (V-b)	$H\,V^{2-\varepsilon}$	p	H (V-b)	$H\,V^{2-\varepsilon}$
atm.		$2-\varepsilon=1.903$	atm.		$2-\varepsilon=1.912$	atm.		$2-\varepsilon=1.912$
83	0.0171	1.56	110.5	0.0181	1.66	120	0.0188	1.72
72	0.0172	1.54	104	0.0179	1.64	112	0.0183	1.67
59	0.0177	1.55	96	0.0180	1.63	104	0.0181	1.64
			90	0.0172	1.58	93	0.0179	1.60
mean	0.0173	1.55	82	0.0175	1.56	87	0.0182	1.62
			80	0.0172	1.53	84	0.0183	1.62
			76	0.0174	1.52	80	0.0186	1.65
			74	0.0170	1.51	76	0.0187	1.67
			73	0.0170	1.50	75	0.0192	1.74
			72	0.0171	1.52			
						mean	0.0185	1.66
			mean	0.0174	1.57			

35°C			40°C		
p	H (V-b)	$H\,V^{2-\varepsilon}$	p	H (V-b)	$H\,V^{2-\varepsilon}$
atm.		$2-\varepsilon=1.913$	atm.		$2-\varepsilon=1.915$
114.5	0.0183	1.64	112	0.0177	1.57
109	0.0181	1.63	108	0.0176	1.56
96	0.0184	1.63	100	0.0180	1.59
88	0.0181	1.61	94	0.0181	1.62
85	0.0175	1.56			
			mean	0.0179	1.59
mean	0.0181	1.61			

Total average value of H (V-b), 0.0178 with 2.8% deviation; total average value of $H\,V^{2-\varepsilon}$, 1.60 with 2.7% deviation.

6) A. J. Batschinski, *Z. phys. Chem.*, **84**, 643 (1913).

According to Batschinski's formula[6] for normal liquids, the product of viscosity coefficient η by specific free volume $(v-\omega)$ is independent of temperature, where $M\omega$ (M= molecular weight) is nearly equal to van der Waals' b ($=V_c/3$). His formula can be rewritten as follows: $\eta(V-b)$=a constant independent of temperature where V is the molecular volume. Applying the latter formula to Phillips' viscosity data, we find that the formula holds good at high pressures for the measured temperature even above the critical temperature, and further, a like constancy is also obtained if we assume η to be simply proportional to cohesive pressure, a/V^{2-6}, in the author's equation (see Table 1).

Moreover, between the constant range of $\eta(V-b)$ or ηV^{2-6} at each temperature (see Table 1) and its corresponding superheated liquid portion of the author's curve (see Fig. 2) there may exist a parallelism, or in other words, the lowest pressure limit of the former appears to come near the end point (close to the minimum) of the latter.

The above results lead to the conclusion that the occurrence of a superheated liquid portion above the critical temperature is necessary for elucidating the persistence of a liquid molecular state above the critical temperature, which no equation except the author's presents, this phenomenon being also in accord with the recent Swietoslawski and Markowska's observation on the critical region, that density difference between the lower and upper parts of the tube was still noticeable after the disappearance of the meniscus[7].

The author is indebted to Nagasaki American Cultural Center for furnishing him with American journals in which Beattie and his coworkers published their compressibility measurements.

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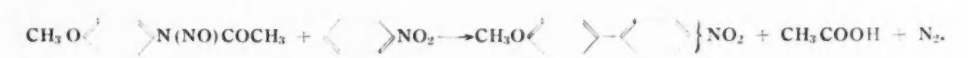
7) W. Swietoslawski, H. Markowska, *Roczniki Chem.*, **26**, 207 (1952); *C.A.* **47**, 10302 (1953).

Influence of Substituent Groups on Nuclear Reactivity in Formation of Substituted Biphenyls through Reactions of Aromatic Diazo and Cognate Compounds with Aromatic Liquids. III. The Substitution of Nitrobenzene by the p-Anisyl Radical

By Osamu SIMAMURA and Toshihiko MIGITA

(Received March 22, 1954)

In a previous paper[1] in this series, it has been shown that the ortho, para and even meta positions of nitrobenzene are activated by the nitro group over the benzene nucleus itself towards the substitutive attack by the phenyl radical produced by the decomposition of N-nitrosoacetanilide or of benzenediazo hydroxide, the order of the reactivities of the three isomeric positions being para> ortho>meta. Augood, Hey and Williams[2] have later reported on the phenylation of nitrobenzene by the decomposition of benzoyl peroxide, the trend of the influence of the nitro group being similar to that found in the above investigation. It seemed of interest to examine how a substituent placed in the phenyl radical alters the nature of the influence of the substituent in an aromatic compound to be attacked by the radical. The present paper deals with the results of experiments on the substitution of nitrobenzene by the *p*-anisyl radical formed by the decomposition of N-nitroso-*p*-acetanisidide, which yields isomeric nitro-4-methoxybiphenyls as follows:



1) O. Simamura, T. Inukai and M. Kanazashi, This Bulletin, **23**, 205 (1950).

2) D. R. Augood, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, **1952**, 2094.

N-Nitroso-*p*-acetanisidide (7.6 g., 0.04 mol.) was decomposed at room temperature in 246 g. (2 mol.) of nitrobenzene giving 0.82 g. of 4-methoxy-4′-nitrobiphenyl, m. p. 110°, and 1.29 g. of 4-methoxy-2′-nitrobiphenyl, m. p. 60° (for the identification of these compounds see the experimental part). When 15 g. (0.077 mol.) of N-nitroso-*p*-acetanisidide was decomposed in a mixture of 288 g. (2.34 mol.) of nitrobenzene and 360 g. (4.62 mol.) of benzene and the reaction mixture worked up as described in the experimental part, 4-methoxybiphenyl, 4-methoxy-4′-nitrobiphenyl and 4-methoxy-2′-nitrobiphenyl were obtained in yields of 2.56 g., 2.38 g. and 3.85 g., respectively, that is, in a millimolar ratio of 13.9 : 10.4 : 16.8. The ratio of the two isomeric methoxynitrobiphenyls formed in the competitive reaction in a mixture of nitrobenzene and benzene was thus found to be in good agreement with that in the reaction in nitrobenzene alone. Any trace of 4-methoxy-3′-nitrobiphenyl could not be detected in the product from this reaction.

On the basis of the molar ratio in which the products were formed and of the amount of the reactants competing for the radical the relative reactivities[1] of the ortho, meta and para nuclear positions of nitrobenzene towards the *p*-anisyl radical are calculated to be 7.24, 0, and 8.95, respectively the reactivity of one nuclear position of benzene itself towards the same radical being taken as unity. These values are compared with the corresponding ones for the reactivity towards the phenyl radical (see Table I); it is noted

TABLE I

RELATIVE REACTIVITIES OF THE ISOMERIC NUCLEAR POSITIONS OF NITROBENZENE.

Source of radical	Relative reactivity			Reference
	o	*m*	*p*	
N-Nitroso-*p*-anisidide	7.24	0	8.95	Present work
Diazotized aniline	6.6	2.8	11	(1)
N-Nitrosoacetanilide	15–5.4	5.8	9.8–30	(1)
Dibenzoyl peroxide	7.0	1.2	7.9	(2)

that the trend is alike in both cases, as far as the ortho and para positions are concerned. The meta position of nitrobenzene is, however, completely unreactive towards the attack by the *p*-anisyl radical whereas it is a little more reactive towards the attack by the phenyl radical than benzene itself. It is generally known that the methoxyl group exerts a polar effect on the para carbon atom, which tends to increase electron density at that atom. On the other hand the polar effect of the nitro group is to decrease electron density at the positions ortho and para to the nitro group below that in the benzene nucleus. Accordingly, it might be expected from a simple electrostatic consideration that the substitution by the *p*-anisyl radical will take place preferentially at the ortho and para positions of nitrobenzene. Further, with an electron-releasing methoxyl group in 4 and an electron-attracting nitro group in 2′ or 4′ position, the biphenyls produced will be more stabilized than otherwise, since such a relative orientation of both groups makes possible their mesomeric conjugation with each other; a resulting gain in extra resonance energy will contribute in lowering the energy of activation for the formation of these isomers. All these considerations point to the preponderant formation of 2- and 4-nitro-4′-methoxybiphenyls. However, as is evident from the comparison of the reactivity values towards the *p*-anisyl with those towards the phenyl radical, the effect due to the co-operation between the *p*-methoxyl group in the attacking radical and the nitro group in the molecule being attacked appears to be very small, if any. In view of both this apparent ineffectiveness of the *p*-methoxyl group in influencing the course of the reaction and the considerable reactivity of the meta position of nitrobenzene towards the phenyl radical, the *p*-anisyl radical is excepted to attack also the meta position of nitrobenzene to an appreciable extent. The reason why 4-methoxy-3′-nitrobiphenyl should actually have not been formed is not clear.

Experimental

Materials N-Nitroso-*p*-acetanisidide was prepared according to Haworth and Hey[3] by the action of nitrous fumes on *p*-acetanisidide in a mixture of acetic acid and acetic anhydride cooled with ice. The resulting dark green solution was poured into a mixture of ice and water with vigorous stirring, and the pale yellow precipitate of N-nitroso-*p*-acetanisidide was collected, washed

3) J. W. Haworth and D. H. Hey, *J. Chem. Soc.*, **1940**, 361.

well with water and dried on a porous plate. Nitrobenzene was purified by distilling commercial nitrobenzene in steam, fractionating through a Vigreux column under reduced pressure, and finally crystallizing the distillate and discarding the liquid portion. Benzene was purified by shaking with concentrated sulfuric acid and then by fractionating through a Vigreux column.

Decomposition of N-Nitroso-*p*-acetanisidide in Nitrobenzene N-Nitrosoacetanisidide (7.6 g., 0.04 mol.) was added to 246 g. (2 mol.) of nitrobenzene at room temperature. The solution turned red in ten minutes and the evolution of nitrogen began, which continued for about one hour. After standing two days, the reaction mixture which had become dark brown was distilled under diminished pressure to remove nitrobenzene. Steam-distillation of the residue (10 g.) at 145° gave 3.2 g. of a distillate, which solidified on standing. This was separated into 0.82 g. of 4-methoxy-4'-nitrobiphneyl, yellow needles, m. p. 110° (from alcohol) (Found: N, 6.18; mol. wt., 231 (Rast). Calculated for $C_{13}H_{11}NO_3$: N, 6.11%; mol. wt., 229.2), and 1.29 g. of 4-methoxy-2'-nitrobiphenyl, yellow prisms, m. p. 60° (from alcohol) (Found: N, 6.31; mol. wt., 235 (Rast). Calc. for $C_{13}H_{11}NO_3$: N, 6.11%; mol. wt., 229.2). The separation was carried out by growing large crystals of the isomers, which could easily be distinguished from each other, from an alcoholic solution and sorting them out. Repeated operations of this procedure gave finally an inseparable mixture, a further separation of which was effected by a chromatography on alumina with a method of fractional elution according to Reichstein and Shoppee.[4]

Identification of Methoxynitrobiphenyls One of the above methoxynitrobiphneyls, m. p. 110°, was identified as 4-methoxy-4'-nitrobiphenyl by oxidizing 0.08 g. of it with 0.4 g. of chromic anhydride in acetic acid on a hot water bath to *p*-nitrobenzoic acid.

The oxidation of another isomer, m. p. 60°, gave no isolable product. A synthetic method was therefore followed. Aqueous sodium hydroxide was added dropwise to a stirred mixture of 100 cc. of anisole and diazotized *o*-nitroaniline (5 g.) in dilute sulfuric acid and the mixture stirred for a further one hour. The anisole layer was separated, the anisole removed under diminished pressure, the residue distilled with superheated steam, giving 0.8 g. of reddish brown distillate, which on distillation in vacuo gave a fraction, b. p. 110° at 5 mm. Hg. When this was dissolved in hot alcohol and the solution let stand, 0.1 g. of yellow crystals was deposited, which on recrystallization from alcohol gave the same compound m. p. 60-61°, as the above methoxynitrobiphenyl, the mixed melting point showing no depression. Of the theoretically possible isomers of methoxy-2-nitrobiphenyls to be produced by this synthesis only 4'-methoxy compound can also be a product from the decomposion of N-nitroso-*p*-acetanisidide in nitrobenzene. Thus, they were identified as 4'-methoxy-2-nitrobiphenyl.

Decomposition of N-Nitroso-*p*-acetanisidide in a Mixture of Benzene and Nitrobenzene N-Nitrosoacetanisidide (1.5 g., 0.077 mol.) was added to a mixture of 360 g. (4.62 mol.) of benzene and 288 g (2.34 mol.) of nitrobenzene. The reaction took place as described for the run in nitrobenzene alone. Benzene and nitrobenzene were removed from the reaction mixture under diminished pressure yielding 32 g. of residue, which gave 4.2 g. of solid (A) and further 10.2 g. of partly solidified distillate (B) on steam-distillation at 120 to 200°. Fraction A gave 4-methoxybiphenyl, m. p. 88°, on recrystallization from alcohol. The solid substance in B was identified with 4-methoxy-4'-nitrobiphenyl. The separation of the two isomers was carried out as before first by sorting out crystals and then by chromatography of the residues from mother liquors of all recrystallizations. Thus the crystalline product isolated were in all 2.56 g. of 4-methoxybiphenyl, 2.38 g. of 4-methoxy-4'-nitrobiphenyl and 3.85 g. of 4-methoxy-2'-nitrobiphenyl. Further, the chromatography yielded 0.70 g. of a brown oil, which could not be crystallized. As it was suspected that the missing isomer, 4-methxy-3'-nitrobiphenyl, might be present in this oil, it was treated with potassium permanganate in pyridine, but no acidic substance was isolated. The action of 0.18 g. of anhydrous aluminium chloride on 0.3 g. of this oil in 100 cc. of nitrobenzene below 120° followed by decomposition with water produced no crystalline compounds. The oily product was dissolved in alkali, heated with 0.3 g. of potassium permanganate, the mixture acidified and extracted with ether. The ethereal solution was shaken with aqueous sodium carbonate, and the aqueous layer gave traces of benzoic and *o*-nitrobenzoic acids on acidification. *m*-Nitrobenzoic acid could not be detected.

Summary

The decomposition of N-nitroso-*p*-acetanisidide in nitrobenzene at room temperature yielded 4-methoxy-4'-nitrobiphenyl and 4-methoxy-2'-nitrobiphenyl in a ratio of 1:1.6. From the result of a similar experiment in a mixture of nitrobenzene and benzene, which compete for the *p*-anisyl radical produced

4) T. Reichstein and C. W. Shoppee, *Discussions Faraday Soc.*, No. 7, 305 (1949).

from N-nitroso-*p*-acetanisidide, the relative reactivities of the ortho, meta and para positions of nitrobenzene towards the *p*-anisyl radical are found to be 7.24, 0, and 8.95, respectively, the reactivity of one nuclear position of benzene towards the same radical being taken as unity.

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Some Observations on the Reactions of α,α'-Dimethylstilbene and Related Compounds

By Osamu SIMAMURA and Hiroshi SUZUKI[1]

(Received February 23, 1954)

F. v. Wessely and H. Welleba[2] reported that α,α'-dimethylstilbene of m. p. 67° was not isomerized to the geometrical isomer by the action of iodine in benzene solution. Therefore in view of the well established fact that thermally or photochemically activated halogen can cause the cis-trans interconversion of various ethylenic compounds, it seemed of interest to study the actions of various agents which are known to be effective in causing the stereoisomerization of the ethylenic compound on the geometrical isomers of α,α'-dimethylstilbene.[3] The present paper gives an account of some observations made during this investigation.

Ramart-Lucas and Salmon-Legagneur[5] heated α,α'-dimethylstilbene with a little concentrated sulfuric acid and found that the isomerization of the trans to the cis isomer took place only to a very limited extent, but that the reverse reaction could not be effected. The re-examination of the action of sulfuric acid (for 20 hours at 210°) revealed that the isomerization, in fact, occurred from either isomer yielding an equilibrium mixture consisting of about 55% of the trans and 45% of the cis isomer. The implication of this result has already been discussed[4] in terms of the steric effect of substituents on the stabilization of the molecule due to the conjugation of unsaturated systems.

We repeated Wessely and Welleba's experiment[2] by boiling 0.1 g. of *cis*-dimethylstilbene and 14 mg. of iodine in 5 cc. of benzene for 4.5 hours and recovered the unchanged material, thus confirming their results. H. J. Barber et al.,[6] however, effected the isomerization of *cis*-4,4'-dibromo-α,α'-dimethylstilbene to the trans isomer by boiling in the presence of traces of iodine in nitrobenzene. When trans-α,α'-dimethylstilbene was heated at 210° for 19 hours with a little iodine an oily product was formed, from which 22% of *meso*-2,3-diphenylbutane[7], m. p. 129-129.5°, was isolated. The cis isomer gave the same result. In none of the experiments carried out was any isomerized product detected. Part of α,α'-dimethylstilbene was apparently hydrogenated at the ethylenic double bond by the action of iodine at the expense of the remainder. No products expected from the dehydrogenation could be isolated. A similar treatment of stilbene with iodine yielded 38% of bibenzyl.

As evidence has been obtained to show that bromine atoms can isomerize dimethyl-

1) Present address: The College of General Education, Tokyo University.

2) F. v. Wessely and H. Welleba, *Ber.*, **74**, 777 (1941).

3) α,α'-Dimethylstilbene exists in two geometrically isomeric forms, one with m.p. 107° and the other with m.p. 67°; the former was assigned the trans and the latter the cis configuration on the basis of the dielectric constant measurements by Wessely and Welleba[2], but relevant numerical data have never been available. Recently, a confirmation of this assignment has been obtained by one of us[4] from theoretical considerations concerning the ultraviolet absorption spectra of the two isomers; accordingly, in this paper the higher melting isomer will be designated as the trans and the lower melting one as the cis isomer.

4) H. Suzuki, This Bulletin **25**, 145 (1952).

5) Ramart-Lucas and Salmon-Legagneur, *Bull. Soc. Chim. France*, [4] **45**, 718 (1929).

6) H. J. Barber, R. Slack and A. M. Woolman, *J. Chem. Soc.*, **1943**, 99.

7) A small amount of this substance was also obtained as a by-product in the reduction of 3,3-diphenyl-2-butanone with sodium and alcohol to 3,2-diphenyl-2-butanol in the course of an attempted synthesis of dimethylstilbene from acetophenone. W. Thörner and Th. Zincke (*Ber.*, **11**, 1988 (1878)) claimed to have prepared 2,2-diphenylbutane, m.p. 127.5~128.5°, by the action of phosphorus and hydrogen iodide on acetophenone and pointed out the identity of the substance with 2,3-diphenylbutane formed from (1-bromoethyl)benzene by the action of zinc or sodium (Br. Radziszewsky, *Ber.*, **7**, 140 (1874); C. Engler and H. Bethgef, ibid,. **7**, 1125 (1874)). It is highly probable that 2,2-diphenylbutane of Thörner and Zincke is *meso*-2,3-diphenylbutane.

stilbene, as will be described later, it is only because of the steric repulsion exerted by large groups at the ethylenic linkage on an attacking iodine atom which is larger than a bromine atom that iodine is ineffective in causing the isomerization at lower temperatures. On the other hand at higher temperatures, at which the isomerization catalyzed by iodine atoms might take place, the disproportionation of dimethylstilbene by iodine becomes prevailing, so that any isomerization would be completely masked.

According to Barber et al.,[7] *trans*- and *cis*-4,4'-dibromo- α,α'-dimethylstilbenes are different from each other in their behavior towards bromine in chloroform at room temperature; the latter adds bromine to give 2,3-dibromo-2,3-bis-(*p*-bromophenyl)-butane, while the former does not. Further, J. Lévy[8] reported the formation of dibromide, m. p. 150-155°, from dimethylstilbene. The results of the present experiments on the action of bromine are noteworthy. When bromine was added to a carbon tetrachloride solution of *trans*- or *cis*-dimethylstilbene in diffuse room light at night the decolorization occurred and the evolution of hydrogen bromide took place immediately. Thus, one mole of dimethylstilbene consumed ultimately about two moles of bromine, approximately two moles of hydrogen bromide being evolved. Evidently, the substitution by bromine took place rather than the addition to the double bond. The product was, besides traces of α-bromoacetophenone, the same 1,4-dibromo-2,3-dimethyl-2-butene, m. p. 153.5-155°, whether the starting material was the trans or the cis isomer. The structure of this compound, which seems to be identical with that obtained from bromine and 2,3-diphenylbutadiene[9], was established on the basis of analytical data and the result of ozonolysis which gave α-bromoacetophenone. It is probable that Lévy obtained this compound and described it as dimethylstilbene dibromide. The crude product from this reaction, melting at 134-150°, contained some crystals which decomposed with effervescence at about 130°. It is suspected that dimethylstilbene dibromide may have been formed, although it could not be actually isolated. When one mole of bromine was allowed to react with one mole of *trans*-dimethylstilbene in carbon tetrachloride in the dark, about 42% of the dimethylstilbene was converted to a crystalline mixture, melting at about 130° to 150°, the bromine content of which corresponded approximately to the calculated value for 1,4-dibromo-2,3-diphenyl-2-butene, and about 27% was recovered as a crystalline mixture, melting at 50° to 77°, consisting of *cis*- and *trans*-dimethylstilbenes. When a similar experiment was carried out in a quartz flask in direct sunlight, there was a vigorous evolution of hydrogen bromide, giving a complex mixture of products from which 1,4-dibromo-2,3-diphenyl-2-butene (6%) and a small amount of α-bromoacetophenone (as 2,4-dinitrophenylhydrazone) were isolated.

The observation that the cis-trans isomerization of dimethylstilbene took place and that the intervention of oxygen occurred as revealed by the formation of α-bromoacetophenone suggests that the action of bromine on dimethylstilbene involves bromine atoms and, consequently, radicals at some stage of the reaction, because it is well established that bromine atoms induce the cis-trans isomerization of ethylenic compounds, and that the addition of bromine to a double bond can take place through a radical mechanism involving bromine atoms.[10] A bromine atom adds to one carbon atom of the central double bond of dimethylstilbene forming a radical intermediate which contains a single bond between the α,α' carbon atoms. The radical can then react in three ways: (1) cis-trans isomerization by the rotation of the groups round the single bond between the α,α' carbons followed by the expulsion of the bromine atom to regenerate a double bond between the α,α' carbons; (2) reaction with a bromine molecule to give dimethylstilbene dibromide and another bromine atom; and (3) reaction with oxygen to give an oxygenated radical which decomposes in a manner generally postulated for peroxides[11] with the fission of the bond between α,α' carbons producing eventually a molecule of acetophenone which is then brominated to α-bromoacetophenone. The mechanism of the formation of 1,4-dibromo-2, 3-diphenyl-2-butene is not clear. There are two possibilities. One involves dimethylstilbene dibromide and 2,3-diphenylbutadiene as intermediates. Inspection of a model of the former constructed with Taylor-Hirschfelder atom models shows that there is considerable steric strain due to the crowding of the bulky substituent groups. Accordingly dimethylstilbene dibromide may be so unstable a substance as to decompose readily. If any decomposition takes place at a low temperature during the present reaction to yield

8) J. Lévy, *Bull. Soc. Chim. France*, [4] **29**, 878 (1921).
9) C. F. H. Allen, C. G. Eliot and A. Bell, *Can. J. Research*, **17B**, 75 (1939); *C. A.*, **33**, 6284 (1939).
10) O. Simamura, This Bulletin, **17**, 274 (1942).
11) J. E. Leffler, *Chem. Rev.*, **45**, 385(1949); C. E. Frank, ibid., **46**, 155 (1950).

hydrogen bromide and 2,3-diphenylbutadiene, then the latter would give dibromodiphenylbutene through the 1,4-addition with bromine. It is possible that oxygen may intervene at the stage where 2,3-diphenylbutadiene adds bromine, the latter attaching itself to the terminal carbon and oxygen to the α carbon atom, and the subsequent decomposition yielding α-bromoacetophenone. The other mechanism involves the substitution by bromine at the methyl group through a radical chain mechanism; a bromine atom abstracts a hydrogen atom from a methyl group of dimethylstilbene, producing a radical stabilized by a mesomeric structure, which in turn gives, by reacting with a molecule of bromine, 1-bromodiphenylbutene and a bromine atom. That 1-bromodiphenylbutene could not be isolated from the reaction mixture might suggest either that it is substituted by bromine at the remaining methyl group to give dibromodimethylstilbene much more rapidly than dimethylstilbene is substituted to give the monobromo derivative or that the bromine atom is unable to attack the methyl group as postulated above.

The action of bromine on dimethylstilbene leading to the facile substitution at the methyl group rather than the addition at the double bond seemed to be attributable to the steric effect in the molecule caused by the crowding of bulky groups; consequently, in order further to ascertain the effect of substituents in the α,α' positions on the bromination of stilbenes the following experiments were conducted. To a solution of 0.33 millimole of an α,α'-disubstituted stilbene in 5 cc. of carbon tetrachloride was added 0.16 millimole of bromine in carbon tetrachloride (about 0.17 cc.) in diffuse light, and the time required for decolorization was compared. In Table I where the results are summarized, the figures in the column headed I denote the time which had elapsed before the red color of the reaction mixture just matched that of a standard bromine solution in carbon tetrachloride, which was approximately 6 millimolar in bromine; the figures in columns II and III denote the time when the reacting solution was faintly pale yellow and completely colorless, respectively. The number of plus signs in the fifth column indicate the approximate intensity of the evolution of hydrogen bromide visually observed. The values in the last column were determined by separate experiments.

Table I

Action of bromine on various stilbenes

	Consumption of bromine (time in min.)			Evolution of HBr	Approximate number of moles of bromine reacted
	I	II	III		
Stilbene	2-3 (hrs.)	—	—	0	1
trans-α-Methylstilbene	1-2	—	—	++	1
trans-α,α'-Dimethylstilbene	6	10	13	++++	2
cis-α,α'-Dimethylstilbene	7-9	35–45	—	+++	2
α-Methyl-α'-ethylstilbene	30	50	65	++	2
trans-α,α'-Diethylstilbene	40	60	—	+	2
cis-α,α'-Diethylstilbene	60	115	—	+	2
Methyltriphenylethylene	2-2.5 (hrs.)	—	—	+	1

Of the compounds shown in Table I stilbene and methylstilbene add bromine to the double bond, the former more slowly than the latter; this is probably due to the retarding action of atmospheric oxygen. Methylstilbene appears to react faster because a little hydrogen bromide formed by the substitution accelerates the addition of bromine by producing, in co-operation with oxygen, bromine atoms which start the chain addition reaction of bromine[10].

Methyltriphenylethylene did not add bromine, but was substituted at the methyl group only slowly in spite of the evolution of hydrogen bromide; the absence of the addition is probably due to the steric hindrance caused by the large substituents as in the case of tetraphenylethylene which also adds no bromine. The slowness of the substitution is also attributable to the steric hindrance which prevents the double bond from producing bromine atoms from hydrogen bromide and oxygen.

Experimental

Materials Dimethylstilbene was prepared according to Ott[12] by dehydration and rearrangement of 100 g. of 3,3-diphenyl-2-butanol, b. p. 172-3° at 14 mm., n_D^{21} 1.5822 (synthesized by the method of Lévy[8]), by boiling with 13 g. of concentrated sulfuric acid in 400 g. of glacial acetic acid for 20 hours. Recrystallization of the crude product from petroleum ether yielded 34 g. of the trans

12) E. Ott, *Ber.*, **61**, 2135 (1928).

isomer, m. p. 107°. The purification of the cis isomer proved to be difficult. The best method was to grow large crystals and to pick out hexagonal plates in which the cis isomer had crystallized. Repeated recrystallization from petroleum ether gave 10 g. of the cis isomer, m. p. 67–67.3°.

α-Methylstilbene was prepared according to Hell[13] and Ley.[14] Dehydration of 43 g. of 1, 2-diphenyl-2-propanol by doiling with 80 g. of acetic anhydride and 40 g. of acetyl chloride gave an oil containing crystals. The crystals were filtered, and recrystallization from petroleum ether gave 20 g. of *trans*-α-methylstilbene, m. p. 83–83.5° The oily product was fractionally distilled in vacuo to yield 4 g. of an oil, b. p. 151–155° at 14 mm., which consisted mainly of *cis*-α-methylstilbene as revealed by the ultraviolet absorption spectrum.[4]

α-Methyl-α'-ethylstilbene was prepared by the method of Lévy.[5] The isomer which crystallized, m. p. 47–8°, was found to be the trans form by means of the ultraviolet absorption spectrum. The cis isomer could not be freed from contamination with a considerable amount of the trans isomer, as revealed by ultraviolet spectrum,[4] and formed an oily specimen.

α, α'-Diethylstilbene was prepared similarly to the synthesis of the dimethyl analogue. α, α-Diphenylbutyraldehyde, b. p. 185–190° at 18 mm. and ethylmagnesium iodide in ether gave 4, 4-diphenyl-3-hexanol, b. p. 185° at 14 mm., which, boiled with a little concentrated sulfuric acid in glacial acetic acid, yielded an oily mixture of the cis and trans forms, b. p. 166° at 12 mm. On cooling, the oil deposited crystalline trans isomer, which melted at 77–78° after repeated crystallizations from petroleum ether. The mother liquor was further fractionated and gave an oil, b. p. 177–8° at 22 mm., which was shown to consist mainly of *cis*-α, α'-diethylstilbene by measurement of the ultraviolet absorption spectrum.[4]

Methyltriphenylethylene was prepared according to Meisenheimer[15] by the action of phenylmagnesium bromide on 2, 2-diphenylpropanal, b. p. 170° at 15 mm., followed by dehydration and rearrangement of the resulting carbinol with concentrated sulfuric acid. The product melted at 88–9°, b. p. 210° at 14 mm.

Isomerization by Sulfuric Acid *cis*- or *trans*-Dimethylstilbene (about 0.8 g.) was heated for 20 hours at 210° with a few pieces of biscuit chips impregnated with concentrated sulfuric acid in a sealed tube. It was cooled, the crystals were pressed on a porous plate to remove some adhering oily matter, and the isomeric composition of the product was determined by comparing its fusing behavior with that of a standard sample of known composition. The isomerization occurred from either isomer giving an equilibrium mixture consisting of about 55% of the trans and 45% of the cis isomer. No isomerization took place at 100° for 20 hours, and only a slight isomerization in the absence of sulfuric acid at 210° for 20 hours.

13) C. Hell, ibid., **37**, 453 (1904).
14) H. Ley, ibid., **50**, 243 (1917).
15) J. Meisenheimer, *Ann.*, **456**, 126 (1927).

Action of Iodine A sealed tube containing 1.45 g. of *trans*-dimethylstilbene and 0.03 g. of iodine was heated for 19 hours in boiling nitrobenzene. The reaction mixture, taken up in ether (with active charcoal), filtered, and the ether removed from the filtrate, gave an oil, from which 0.315 g. of *meso*-2, 3-diphenylbutane, m. p. 129.0–129.5°, crystallized, the melting point being not depressed on admixture with an authentic specimen prepared by hydrogenating *cis*-dimethylstilbene with one mole of hydrogen in the presence of palladium-barium suffate in ether. An experiment with the cis isomer gave the same result. Similarly stilbene gave 38% of bibenzyl, m. p. 48–51°, identified by the mixed melting point with an authentic specimen.

Action of Bromine Bromine (14.5 millimoles) was added to 1.503 g. of *trans*-dimethylstilbene in 15 cc. of carbon tetrachloride. After decolorization the carbon tetrachloride was removed in vacuo at room temperature and 2.496 g. of a crystalline compound, m. p. 134–150°, was obtained. Repeated crystallizations from carbon tetrachloride gave 0.974 g. of 1, 4-dibromo-2, 3-diphenyl-2-butene, needles, m. p. 153.5–155° (Found: Br, 43.6. Calcd. for $C_{16}H_{14}Br_2$: Br, 43.72%). This substance (0.42 g.),on ozonization in 50 cc. of chloroform followed by decomposition with water, gave 0.41 g. of α-bromoacetophenone. It was observed under a microscope that the crude product melting at 134–150° contained some crystals which decomposed with effervescence at about 130°. It may be suspected that dimethylstilbene dibromide was also formed. In some experiments carried out similarly to those above, the crude product was washed with a little alcohol and the alcoholic solution deposited, on addition of 2, 4-dinitrophenylhydrazine solution, a very small amount of α-bromoacetophenone 2,4-dinitrophenylhydrazone, m. p. 220°.

The action of bromine on *cis*-dimethylstilbene gave similar results. *trans*-Dimethylstilbene (0.375 g., 1.8 millimoles) in carbon tetrachloride, added in the dark with 1.8 millimoles of bromine in the same solvent (1:20), and the solvent removed in vacuo, gave a crystalline mass, which was extracted with petroleum ether. The insoluble residue, melting at 130 to 150°, weighed 0.23 g. (Found: Br, 42.4, Calcd. for $C_{16}H_{14}Br_2$: Br, 43.72%), which on repeated crystallizations from carbon tetrachloride gave 0.138 g. of 1, 4-dibromo-2, 3-diphenyl-2-butene. Evaporations of the petroleum extract gave about 0.1 g. of a crystalline mixture, m. p. 50–77°, consisting of *cis*- and *trans*-dimethylstilbenes.

trans-α-Methylstilbene consumed about 1 mole of bromine with evolution of hydrogen bromide and gave 1, 2-dibromo-1, 2-diphenylpropane, m. p. 126–7°, as isolable compound.

Methyltriphenylethylene reacted with bromine in carbon tetrachloride only slowly in the dark, but, very rapidly in sunlight, about 1 mole of bromine being taken up with the evolution of hydrogen bromide in accordance with the observation of Meisenheimer[15]. The only product isolated was 3-bromo-1, 1, 2-triphenylpropene, m. p. 121° (from petroleum ether).

cis-Diethylstilbene (2.668 g.) in 30 cc. of carbon tetrachloride reacted with nearly 2 moles of bromine in the course of a few days in the dark, hydrogen bromide being evolved. The removal of the solvent gave viscous matter and 0.78 g. of 2,5-dibromo-3,4-diphenyl-3-hexene, m.p. 156–8° (from carbon tetrachloride).

Summary

cis- and *trans*-α,α'-Dimethylstilbene, heated with a little sulfuric acid at 210°, were isomerized to an equilibrium mixture consisting of 55% of the trans and 45% of the cis isomers. Heated with iodine at 210°, they yielded *meso*-2,3-diphenylbutane. The action of bromine produced 1,4-dibromo-2,3-diphenyl-2-butene; under certain experimental conditions the concurrent cis-trans isomerization was observed. This fact, together with the isolation of a small smount of α-bromoacetophenone as a by-product, supports the view that the reaction proceeds by a mechanism involving bromine atoms. The action of bromine on some α,α'-disubstituted stilbenes was examined. The reactions observed were discussed in terms of the steric effect exerted by the bulky groups at the ethylenic linkage.

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The Action of Hydrogen Bromide and Oxygen on α,α'-Dimethylstilbene and Related Compounds

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A combined action of hydrogen bromide and oxygen on ethylenic compounds induces remarkable reactions involving free radicals:[2-6] to mention a few examples which have some bearing on the subject treated in this paper, the action of hydrogen bromide on isostilbene in the presence of oxygen causes the isomerization[3,4] to stilbene, and, if a larger amount of oxygen is present, the formation of stilbene dibromide takes place[2a,4]; and the joint action of hydrogen bromide and oxygen on various ethylenic compounds causes copious liberation of bromine with those compounds which add bromine to the double bond only to a limited extent, as tetraethyl α,γ-dicarboxy-α-bromoglutaconate, and with some of those which will not do so at all, such as dimethyl dimethylfumarate.[5] These reactions are completely inhibited by a small amount of catechol. The action of hydrogen bromide and oxygen on some α, α'-disubstituted stilbene has now been investigated with special reference to the dimethyl derivative, on reactions of which some observations have been reported in a previous paper.[6]

The passage of hydrogen bromide alone (without special measures to exclude air from the apparatus) or of a mixture with oxygen through a solution of *trans*-dimethylstilbene in carbon tetrachloride in the dark at room temperature caused no reaction whatever; but, on the contrary, *cis*-dimethylstilbene, similarly treated with hydrogen bromide, isomerized partly to the trans isomer, crystals melting at 54 to 71° being recovered, and in the presence of a large amount of oxygen, it underwent a profound change giving acetophenone (9 to 20%), α-bromoacetophenone (20 to 28%) and 1,4-dibromo-2,3-diphenyl-2-butene (3 to 4%) (for a typical run see the experimental part, Expt. No. 14). These reactions were completely inhibited by catechol (37 mol.% of dimethylstilbene) added to a reaction mixture beforehand. Thus, the combined action of hydrogen bromide and oxygen caused the same type of reaction with *cis*-dimethylstilbene as observed with stilbene and other ethylenic compounds. A further point of interest is that the ethylenic bond of *cis*-dimethylstilbene was cleaved so easily

1) Present address: The College of General Education, Tokyo University.
2) (a) Y. Urushibara and O. Simamura, This Bulletin, **14**, 323 (1939).
(b) O. Simamura, ibid., **17**, 274, 326 (1942).
(c) O. Simamura and M. Takahashi, ibid., **22**, 60 (1948).
3) Y. Urushibara and O. Simamura, ibid., **12**, 507 (1937).
4) Idem, ibid., **13**, 566 (1938).
5) O. Simamura, ibid., **15**, 292 (1940).
6) O. Simamura and H. Suzuki, ibid., **27**, 231(1954).

at room temperature to give ketones. It was temporarily considered that the remarkable difference in behavior towards hydrogen bromide and oxygen between the cis and trans isomers of dimethylstilbene might be due to some difference in the electronic state of the central double bond arising from a difference in the extent of its conjugation with the two phenyl groups which are twisted out of a coplanar configuration owing to inevitable steric requirements.[7] It soon became evident, however, that the findings had been spurious. It was found that a specimen of *cis*-dimethylstilbene purified by filtering a petroleum ether solution through a chromatographic column of alumina was no more subject to the action of hydrogen bromide and oxygen than the trans isomer. The specimen which reacted with this gas mixture showed no apparent difference from that purified by the chromatographic method, as far as the melting point and the ultraviolet absorption spectrum were concerned, but the former, on standing in a bright diffuse light of summer days, decomposed slightly and the product, when treated with ferrous ammonium sulfate and aqueous ammonium thiocyanate, developed a red color revealing the presence of a peroxidic substance. It was therefore concluded that the *cis*-dimethylstilbene had retained tenaciously, through a series of purification by repeated crystallizations, traces of peroxidic impurities or those impurities which readily yielded peroxides on autoxidation. With the trans isomer, which is less soluble and crystallizes very well, the impurities must have been easily removed by mere recrystallization. Such traces of impurities undoutedly induced the autoxidative decomposition of dimethylstilbene in air producing peroxidic molecules or very reactive intermediates of a free radical nature and thus catalyzed the reaction with hydrogen bromide and oxygen. It was indeed demonstrated by separate experiments that traces of a peroxide can in fact catalyze the combined attack by hydrogen bromide and oxygen on dimethylstilbene. Thus, in the presence of traces of bonzoyl peroxide the passage of hydrogen bromide through a solution of *trans*-dimethylstilbene in carbon tetrachloride in the dark produced a mixture of the cis and trans forms (Expt. No. 55); if oxygen was passed simultaneously, the cleavage of the double bond occurred yielding the same products (Expt. No. 27) as in the case of the impure *cis*-dimethylstilbene. Similarly, traces of the impure specimen could catalyze the reaction of *trans*-dimethylstilbene. Catechol inhibited these peroxide catalyzed reactions, a fact which is in accord with the view that reactions resulting from the action of hydrogen bromide and oxygen on the ethylenic compounds involves a radical mechanism.

An agent which initiates these reactions is obviously a bromine atom produced from benzoyl peroxide and hydrogen bromide. It adds to one carbon atom of the central double bond of dimethylstilbene forming a radical intermediate which contains a single bond between the α, α' carbon atoms. The radical can then react in the following ways. The first is the cis-trans isomerization by rotation of the groups round the single bond between the α, α' carbons followed by expulsion of the bromine atom to regenerate a double bond between the α,α' carbons. The second is a reaction with oxygen to give an oxygenated radical, which, immediately or after the formation of a hydroperoxide by abstracting a hydrogen atom from hydrogen bromide and leaving a bromine atom, decomposes in a manner generally postulated for peroxides[8] to give eventually acetophenone and fragments of radical nature. The latter are assumed to react with hydrogen bromide producing bromine atoms. Bromine atoms produced in the several ways just mentioned can again attack the double bond of dimethylstilbene continuing the chain process or combine with one another to give bromine molecules. Thus, the formation of brominated compounds such as 1,4-dibromo-2,3-diphenyl-2-butene and bromoacetophenone is readily understood as discussed in the previous report. The inhibitive action of catechol consists in the annihilation of chain carrying bromine atoms.

Ordinary ethylenic compounds are liable to the combined action of hydrogen bromide and oxygen leading to a complicated reaction, because in their presence bromine atoms can be formed from hydrogen bromide and oxygen, thus initiating chains carried by bromine atoms. Both *cis*- and *trans*-dimethylstilbenes undergo no such reaction in the absence of a catalyst, because they are unable by themselves to produce bromine atoms from hydrogen bromide and oxygen. This is probably attributable to the steric effect of the two phenyl and the two methyl groups, which hinder the approach of hydrogen bromide and oxygen to the double bond. On the other hand, once bromine atoms have been produced from hydrogen bromide and a peroxidic initiator, they are active enough, in spite of the steric repulsion, to attack the double bond of

7) H. Suzuki, This Bulletin, **25**, 145 (1952).

8) For a leading reference see J. E. Leffler, *Chem. Rev.*, **45**, 385 (1949) and C. E. Frank, ibid., **45**, 155 (1950).

dimethylstilbene, as has previously been demonstrated,[5] producing radicals which then give the isomerized product or further react with oxygen and hydrogen bromide resulting in the oxidative cleavage of the double bond.

What is of interest in connection with these observations is that, when traces of bromine was added to a solution of *trans*-dimethylstilbene through which hydrogen bromide was being passed, the cis-trans isomerization occurred, and similarly, when a mixture of hydrogen bromide and oxygen was passed in the presence of bromine, the cleavage of the double bond took place (Expt. No. 33). The action of bromine on dimethylstilbene gives 1, 4-dibromo-2, 3-diphenyl-2-butene.[5] When oxygen was passed through a reaction mixture while bromine was being added, the yield of the dibromo-compound decreased and the formation of ketones resulting from the oxidative cleavage of the double bond was observed (Expt. No. 20). That these ketones were not formed from the 1, 4-dibromo-2, 3-diphenyl-2-butene by the action of oxygen and the hydrogen bromide primarily produced from bromine and dimethylstilbene was demonstrated by a separate experiment, in which the dibromo-compound was recovered unchanged when subjected to the action of oxygen and hydrogen bromide, even in the presence of benzoyl peroxide or of bromine. These observations are readily explained on the basis of the radical nature of the action of bromine on dimethylstilbene as has been pointed out in the previous report.[5] Thus, some radicals formed in the course of the reaction between bromine and dimethylstilbene release the combined attack by hydrogen bromide and oxygen.

The action of hydrogen bromide and oxygen on some other α,α'-disubstituted stilbenes was also examined. *trans*-Diethylstilbene reacted with a mixture of hydrogen bromide and oxygen only in the presence of bromine or of benzoyl peroxide, producing the same type of cleavage of the central double bond as in the case of the dimethyl analogue (Expt. No. 97). The cis isomer was cleaved without added catalyst; the material used boiled at 177–8° at 22 mm. Hg, and probably contained some peroxidic impurities as no special measures of purification had been taken in the preparation. 1, 1, 2-Triphenylpropene did not react with hydrogen bromide and oxygen even in the presence of bromine or of benzoyl peroxide. The action of hydrogen bromide and oxygen on *trans*-α-methylstilbene gave 1, 2-dibromo-1, 2-diphenylpropane, corresponding to stilbene dibromide from stilbene, along with benzoic acid and α-bromoacetophenone (Expt. No. 69). The results of these experiments substantiate the view put forth above, that some molecule with a double bond sterically hindered to such an extent that it can not by itself initiate the chains involving bromine atoms is able to react with bromine atoms and propagate the chains. Further, the absence of reaction with 1, 4-dibromo-2, 3-diphenyl-2-butene and 1, 1, 2-triphenylpropene demonstrates that the steric hindrance is so great in these molecules that they are not only incapable of such initiation, but unsusceptible even to the action of bromine atoms or, if a bromine atom adds to the double bond, unable to propagate the chains efficiently.

Experimental

The stilbenes used in this study were prepared as reported previously.[6] Hydrogen bromide was generated by dropping dried bromine on hot tetralin, passed through a bottle of cooled tetralin and a tube filled with glass wool and anthracene and then dried by passage over phosphorus pentoxide.

Typical experiments which have been referred to in the discussion are described in the following. All reactions were carried out in the dark below room temperature (0 to 10°).

Expt. No. 14 *cis*-Dimethylstilbene (0.140 g.) was dissolved in 10 cc. of carbon tetrachloride and hydrogen bromide was passed for 45 minutes into the solution. The solvent was removed under diminished pressure, the oily residue containing a small amount of crystals was treated with alcohol to dissolve the oil; the crystals were collected on a filter and identified with 1,4-dibromo-2,3-diphenyl-2-butene, m. p. 147-152° (yield 10 mg.), which was not depressed on admixture with the specimen prepared from bromine and dimethylstilbene. The alcoholic extract, on treatment with 2, 4-dinitrophenylhydrazine deposited 0.18 g. of yellowish brown precipitate (Found: Br, 16.25. Calcd. for $C_{14}H_{11}BrN_4O_4$: Br, 21.11%). This was separated into two components, 2, 4-dinitrophenylhydrazones of acetephenone and α-bromoacetophenone, m. p. 250° and 220°, respectively, by fractional crystallization from alcohol. On the basis of the bromine content of the original mixture, the amounts of the ketones produced were estimated at 0.0735 g. of bromoacetophenone and 0.016 g. of acetophenone.

Expt. No. 20 A solution of bromine in carbon tetrachloride (1 : 20) was added gradually to 0.199 g. of *trans*-dimethylstilbene in 10 cc. of carbon tetrachloride simultaneously with the introduction of oxygen. The reaction mixture, worked up as Expt. No. 14, gave 97 mg. of 1, 4-dibromo-2, 4-diphenyl-2-butene and 0.22 g. of 2, 4-dinitrophenylhydrazone of ketones.

Expt. No. 27 The action of hydrogen bromide and oxygen on 0.226 g. of *trans*-dimethylstilbene and 11 mg. of benzoyl peroxide in 10 cc. of carbon tetrachloride for one hour, worked up as above, yielded 12 mg. of 1, 4-dibromo-2, 3-diphenyl-2-butene

and ketones (0.282 g. of 2,4-dinitrophenylhydrazones).

Expt. No. 33 A mixture of hydrogen bromide and oxygen was passed into 0.13 g. *trans*-dimethylstilbene in 10 cc. of carbon tetrachloride and a few drops of carbon tetrachloride solution of bromine (1:20) was added through a fine capillary tube; the passage of the gas mixture was continued for a further forty-five minutes and the solution was worked up as above to give 5 mg. of 1,4-dibromo-2,3-diphenyl-2-butene and ketones (0.202 g. of 2,4-dinitrophenylhydrazone).

Expt. No. 55 Hydrogen bromide was passed through a solution of 0.102 g. of *trans*-dimethylstilbene, m.p. 107°, and 4 mg. of benzoyl peroxide in 10 cc. of carbon tetrachloride for one hour; the removal of the solvent gave a mixture of the cis and trans isomers melting over a range of 72° to 102°.

Expt. No. 69 A mixture of hydrogen bromide and oxygen was passed for one hour into a solution of 0.267 g. of α-methylstilbene, m.p. 83-83.5°, in 10 cc. of carbon tetrachloride. The mixture was shaken with dilute aqueous sodium carbonate and the aqueons layer deposited benzoic acid on acidification with sulfuric acid (the total yield of the benzoic acid, 18 mg.). The dried carbon tetrachloride solution, concentrated under diminished pressure, gave 0.134 g. of α-methylstilbene dibromide, m.p. 127°, and an oily matter which gave 0.132 g. of 2,4-dinitrophenylhydrazone, m.p. 205-216°, probably of impure α-bromoacetophenone.

Expt. No. 97 A mixture of hydrogen bromide and oxygen was passed into a solution of 0.107 g. of *trans*-α,α'-diethylstilbene, m.p. 77-8°, and 4 mg. of benzoyl peroxide in 10 cc. of carbon tetrachloride for one hour; the mixture was worked up as above to give 0.012 g. of 2,5-dibromo-3,4-diphenyl-3-hexene, m.p. 155-7°, and ketones (0.046 g. of 2,4-dinitrophenylhydrazone). A catalytic action of bromine was demonstrated by an experiment similar to Expt. No. 33.

Summary

The action of hydrogen bromide on *cis*- or *trans*-α,α'-dimethylstilbene in the presence of a peroxidic substance or of bromine in carbon tetrachloride in the dark below room temperature caused a partial isomerization to the respective geometrical isomers. The reaction was inhibited by catechol. When oxygen was allowed to react simultaneously under otherwise the same experimental conditions, the cleavage of the central double bond took place yielding acetophenone and α-bromoacetophenone along with 1,4-dibromo-2,3-diphenyl-2-butene. Similar experiments with α-methylstilbene and α,α'-diethylstilbene were conducted. The action of oxygen and bromine on α,α'-dimethylstilbene caused the same oxidative cleavage of the double bond as with hydrogen bromide and oxygen. It was pointed out that an ethylenic compound which is sterically hindered to such an extent that it is unreactive towards molecular reagents can be reactive enough towards radical reagents.

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The Effect of Conversion on the Mechanism of Vinyl Polymerization. II. Methyl Methacrylate

By Saburo FUJII

(Received March 18, 1954)

In the first paper of this series[1] the author described the application of the photochemical method to the study of vinyl polymerization at various conversions and reported the results on styrene not containing any initiator or chain-transfer substance at room temperatures. It was noted there that the course of polymerization was accompanied by the strong rate acceleration, an extreme increase in kinetic chain lifetime and considerable decrease in apparent activation energy and in the reaction order of chain termination. Those kinds of kinetic behaviour could be explained by the supposition that, with increasing conversion of the system, the mutual termination of polystyrene radicals becomes diffusion-controlled or prevented by the shielding effect of the polymer network.

The author has now applied the same method to methyl methacrylate in an attempt to compare it with the above results on styrene[1]

1) S. Fujii, This Bulletin **27**, 216 (1954).

and with those found by several authors[2,3,4,5,6(a)] for the polymerization of methyl methacrylate in the later stages. This paper reports and discusses the results obtained under the analogous conditions as described in the first paper.[1]

Experimental

Commercial methyl methacrylate was purified by successive washing with dilute sulphuric acid, dilute sodium hydroxide and distilled water, and was dried with calcium chloride over a day. Then it was distilled three times through a fractionating column of 1 meter long at 105 mm. pressure, and the fraction boiling at 45.1°C. was collected and stored in an evacuated flask in the dark. This product was allowed to polymerize to about 10% at 100°C. under the irradiation of ultra-violet light longer than 3300 Å., and then the residual monomer was redistilled with dry ice into a dilatometer used for rate measurements. This operation was carried out in an all glass system evacuated to 10^{-3} mm. pressure. All of the above treatments were necessary to obtain the pure monomer completely free from impurity which may sensitize or retard the polymerization. Unless otherwise noticed, neither photosensitizer nor thermal initiator was added to the reaction system.

The experimental apparatus and procedure were essentially those described in the first paper.[1] The filteration of light from the mercury lamp and the maximum intensity of 3660 Å. light at the front of the reaction cell (4×10^{-8} Einsteins/sec.) were the same as those in the previous experiment.[1] The photo-polymerization was mainly caused by the light of 3660Å., at which wave-length the absorption by the monomer is very little (the molecular extinction coefficient is of the order of 10^{-3})[7], so that the concentration of the radicals within the cell must be uniform. The free radical initiation by the light-excited polymer must be negligible, for the polymer shows no absorption band in the neighborhood of 3660 Å.[8] The rates of photo-and thermal-polymerizations were followed dilatometrically and computed by the use of Matheson's data[6(a)] on the densities of the monomer and the polymer in monomer. In the same manner as described in ref. (1), all the rate measurements were corrected for the thermal reaction taking place in the unilluminated appendages to the cell. The kinetic chain lifetimes at low conversions (of the order of seconds) were measured with a rotating sector, while those at high conversions were estimated from the photochemical after-effects, which were easily observed dilatometrically. After the experiments at low conversions, the reaction system was polymerized to a desirable conversion under the intense irradiation of 3660 Å. light, left alone at room temperature over half a day, and then the experiments at high conversions were carried out.

The main different feature from styrene was the fact that the polymerization of methyl methacrylate by the same light intensity is much faster (about seven times) than that of styrene in spite of the smaller extinction coefficient. To avoid the undesirable temperature elevation and change of conversion in the reaction system, therefore, the rates of photo-polymerization at high conversions were reduced with calibrated screens. The stationary light rates at high conversions were measured after the long period of preliminary illumination.

Results

The polymerization rates and the reaction order of chain termination—The stationary rates of photo-polymerization at three different temperatures were measured at low conversions under the full intensity (4×10^{-8} Einsteins/sec.) of light from the lamp and at high conversions under the intensities reduced with calibrated screens. Table I shows the data obtained on light rate V_{pL}, thermal rate V_d, and the apparent activation energy, E_{app}, of polymerization.

TABLE I

RATES OF PHOTO- AND THERMAL-POLYMERIZATIONS AND OVER-ALL ACTIVATION ENERGIES FOR METHYL METHACRYLATE

Transmission of screen, %	Conversion %	30°C.	40°C.	50°C.	E_{app} kcal./mol.
	(a) Light rate (unit; 10^{-6} mol./l./sec.)				
100	0~1	7.94	11.0	14.1	5.6
27.4	27±1	32.9	41.9	53.4	4.7
12.0	52±2	43.1	54.6	65.8	4.1
	(b) Thermal rate (unit; 10^{-6} mol./l./sec.)				
	0~1	0.29	0.48	0.81	10.1
	27±1	1.58	2.57	3.94	8.9
	52±2	3.49	5.63	8.32	8.5

2) G. V. Schulz and F. Blaschke, *Z. physik. Chemie*, B50, 305 (1941).
3) Trommsdorff, "Coloquium on High Polymers," Freiburg, 1944.
4) G. V. Schulz and G. Harborth, *Die Makromolekulare Chemie*, **1**, 106 (1947).
5) M. H. Mackay and H. W. Melville, *Trans. Faraday Soc.*, **45**, 323 (1949).
6) (a) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *J. Am. Chem. Soc.*, **71**, 497 (1949); (b) ibid., **73**, 1700 (1951); (c) ibid., **73**, 5395 (1951).
7) T. G. Majury and H. W. Melville, *Proc. Roy. Soc. London*, **A205**, 496 (1951).
8) The absorption band of the system shifts to the shorter wave length in the disappearance of vinyl double bond.

This table as a whole shows that the indicated values were reproducible within the error of 10% or less. Also a measurement of light rate in a complete run to 60% conversion was carried out in the same reaction cell at 30°C. under the constant intensity of illumination and the result is shown diagrammatically in Fig. 1. At the same time the reaction order of chain termination, n, i.e., the reciprocal of the intensity exponent of the stationary light rate, was determined in one run in the same reaction cell at several conversions and the results are given in Table II.

TABLE II
THE REACTION ORDER OF CHAIN TERMINATION, n

Conversion %	n
0~1	1.9~2.1
45±2	1.8~1.9
60±2	1.6,~1.8

It is concluded from the above tables and figure that the strong rate acceleration after about 10% conversion is accompanied with some decreases in E_{app} ane n. This kinetic behavior is analogous to that of styrene.[1]

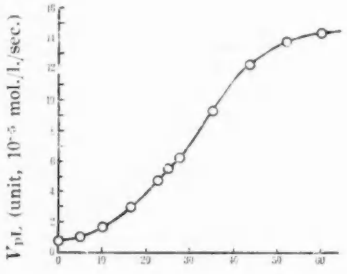

Fig. 1. The rate of photo-polymerization at 30°C. as a function of conversion.

Photochemical after-effect and kinetic chain lifetime—In the measurement of light rates, the reaction showed no detectable induction period in the initial stages, while the prolonged initial- and after-effects were clearly observed in the later stages. Since the rates were followed with a dilatometer, the temperature change of the system in the beginning of illumination and after the interruption of light caused some volume change on the system and more or less disturbed the detection of pure chemical initial- and after-effects. However the ratio of the volume change caused by this undesirable temperature change to the total one by the after-effect became very small at high conversions, so that the allowance for this temperature change was neglected, as the first approximation, in the present discussion of these effects. In a similar manner described in the previous paper,[1] it was confirmed that these effects resulted from an extreme increase in kinetic chain lifetime but not from the decomposition of any unstable substance produced during the previous illumination. A few examples of the observed after-effects are illustrated in Fig. 2, where the relative rate after the interruption of illumination is represented as a function of time.

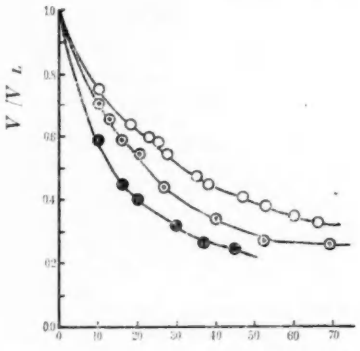

Fig. 2. Photochemical after-effects.

Experimental point	⊙	●	○
Conversion	47%	52%	72%
Temperature	30°C.	50°C.	30°C.
V_{pL}(10^{-5}mol./l./sec.)	4.03	6.58	5.17
V_d/V_{pL}	0.08	0.13	0.48

With several assumptions previously justified[1] and under the case of $n=2$, the mathematical analysis of the photochemical after-effect results in the equation,

$$log\left(\frac{V_p+V_d}{V_p-V_d}\right)=log\left(\frac{V_{pL}+V_d}{V_{pL}-V_d}\right)+\frac{2V_d}{2.303V_{pL}}\times\frac{t}{\tau_s}, \quad (1)$$

and slso the accepted polymerization mechanism leads to the equation,

$$\frac{{}_sV_{pL}}{[M]}=k_p/k_t . \quad \cdots\cdots\cdots\cdots (2)$$

Here V_p is the rate at the time, t, after the interruption of illumination, k_p and k_t the propagation and termination rate constants of growing radicals respectively $[M]$ the monomer concentration and τ_s the average lifetime of kinetic chains at the light rate of V_{pL}, but not the one of each growing radical. Plotting the value of the left hand side of Eq. (1) against the time will lead to a straight

line and then the τ_s value can be estimated from the slope of this line. The k_p/k_t value can be estimated from Eq. (2).

Although the deviation of n from 2 was observed at high conversions as shown in Table II, it may be admitted in the present qualitative discussion that the τ_s and k_p/k_t values at high conversions are estimated, as the first approximation was, by the use of these equations. On the basis of the above, the analytical representations of the observed after-effects are illustrated in Fig. 3, and the τ_s and k_p/k_t values obtained are summarized in Table III.

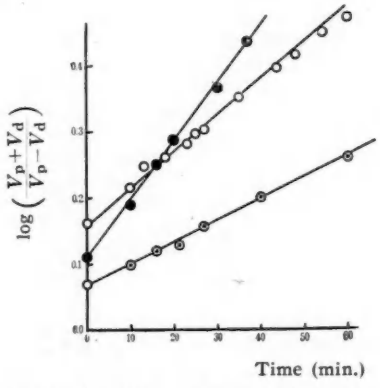

Fig. 3. Analytical representations for the observed after-effects; the experimental conditions for the indicated points are the same as those in Fig. 2.

On the other hand the kinetic chain lifetimes at low conversions were of the order of 10 seconds at the V_{pL} values indicated in Table I, and consequently these were measured with a rotating sector. A typical run in the sector experiments is indicated in Fig. 4, and the initial values of τ_s and k_p/k_t are also summarized in Table III.

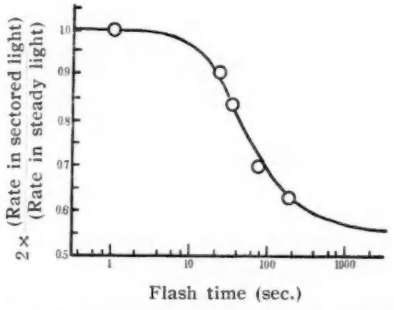

Fig. 4. Rates of polymerization of methyl methacrylate in intermittent light for different times of flash: curve, theory for dark rate 3% of steady light rate; ○, experimental point at 40°C. and steady light rate $=1.06\times10^{-5}$ mol./l./sec.

As noted previously[1,3a] the propagation step in free radical polymerizations has been admitted to be only slightly dependent upon conversion as compared with the termination step, so that the relative decrease in k_t with increasing conversion may be estimated from the k_p/k_t values shown in Table III under the assumption of constant k_p. The evaluated result is indicated in the last column of Table III, and such decrease in k_t is analogous to that previously reported on styrene.

TABLE III

KINETIC CHAIN LIFETIMES AND RATE CONSTANT RATIO IN METHYL METHACRYLATE

Conversion x %	Temp. °C.	V_{pL} mol./l./sec.	τ_s sec.	Av. τ_s at $V_{pL}=10^{-5}$	k_p/k_t	k_{tx}/k_{t0}[b]
0~1	30	3.52×10^{-5}	1.85	[a] 7.43		
		6.83×10^{-5}	1.22			
	30	7.95×10^{-6}	21.7	17.9	1.93×10^{-5}	1
		1.08×10^{-5}	17.2			
	40	1.10×10^{-5}	20.3	22.7	2.47×10^{-5}	
		1.60×10^{-5}	14.5			
47±2	30	4.03×10^{-5}	1260	5080	9.20×10^{-3}	2.10×10^{-3}
52±2	30	4.31×10^{-5}	1098	4730	9.33×10^{-3}	2.07×10^{-3}
	40	5.46×10^{-5}	882	4810	9.48×10^{-3}	
	50	6.58×10^{-5}	762	5010	9.86×10^{-3}	
72±3	30	5.17×10^{-5}	1800	9310	2.96×10^{-2}	6.52×10^{-4}

(a) α-Azo-bisisobutyronitrile sensitizer was used in this experiment; no sensitizer in the others.

(b) The ratio of k_t at x % conversion to its initial value was estimated at 30°C.

Discussion

With the several assumptions previously described,[1] the accepted mechanism of photopolymerization leads to the equation,

$$V_{pL} = (q \varepsilon l I_0)^{1/n} \left(k_p / k_t^{1/n} \right) [M]^{1+1/n} \quad (3)$$

and also, if the thermal initiation of kinetic chains is assumed to be proportional to $[M]^2$,[9] the rate of thermal polymerization may be represented as

$$V_d = k_p \left(\frac{k_t}{k_i} \right)^{1/n} [M]^{1+1/n} \quad (4)$$

Here q is the quantum efficiency of the production of kinetic chains, ε the molecular extinction coefficient of the monomer, l the depth of the reaction cell, I_0 the intensity of illumination and k_i the rate constant of thermal initiation by the monomer. Using these equations and the data in Table III, the rate ratio at 52% conversion to the initial value at 30°C. can be estimated[10] as about 11.8 for V_{pL} and about 8.7 for V_d, while the corresponding experimental ratios are about 17.3 for V_{pL} from Fig. 1 and about 12.0 for V_d from Table I. If the k_{tx}/k_{to} value at 52% conversion is estimated to be half of that indicated in Table III,[11] the differences between the above theoretical and experimental ratios in the rate accelerations may be almost eliminated. Therefore it may be concluded that the observed rate accelerations are attributed to the extreme decrease in k_t. This conclusion has already been suggested by Trommsdorff[4] and several other authors,[2,4,5] who found the catalytic- and photo-polymerizations of several vinyl monomers to be strongly accelerated after certain conversions, and has also been confirmed by Matheson and his co-workers[6a] with the measurement of kinetic chain lifetimes in the biacetyl photosensitized-polymerization of methyl methacrylate at about 33% conversion. Following the data of the latter authors the value of k_{tx}/k_{to} at 33% conversion is in the range $4.6 \sim 6.6 \times 10^{-3}$ at 30°C., while the present work shows about 2×10^{-3} in the neighborhood of 50% at the same temperature. Allowing for the different conversions, one may accept the fact that both the results coincide with each other.

As noted previously on styrene,[1] the observed decreases in k_t and E_{app} with increasing conversion can be explained by the fact that the mutual termination of polymer radicals becomes predominantly diffusion-controlled in the later stages. Using Matheson's datum (2.8 kcal./mole)[6a] for the activation energy of chain termination, E_t, in the initial stages, the observed decrease in E_{app} (=the increase in $1/2\,E_t$) gives about 5.8 kcal./mole[12] for the E_t value at 52% conversion, i.e., the activation energy of the diffusion of polymethyl methacrylate radicals in the reaction system. The E_t values of polystyrene radicals at 38 and 60% conversions have been reported by the present author as about 7 and 9 kcal./mole respectively,[1] and these values are almost in agreement with those estimated from the viscosity equation of Spencer and Williams.[13] Flory[14] reported about 8 kcal./mole as the activation energy of the viscosity for several fused polyesters. Cowley and Melville[15] studied the photo-degradation of polymethyl methacrylate with the rotating sector technique and reported about 20 kcal./mole as the E_t value of the polymer radicals in the fused polymer. Comparing this with the author's data on styrene and Flory's data on polyesters the present value (5.8 kcal.) may be adequate, while the value (20 kcal.) of Cowley and Melville is beyond the accepted order of magnitude for the self-diffusion of polymer in the fused phase.

Some decrease in n observed over about 50% conversion seems to show that, together with the mutual termination of polymer radicals, the self-termination also takes place at very high conversions. Such self-termination may be supposed to be caused by the strong shielding action of a polymer network on the active ends of growing radicals. This suggested mechanism has been discussed in the first paper of this series[1] and supported by Bamford and Jenkins,[16] who studied the photopolymerization of acrylonitrile and found

9) P. J. Flory, *J. Am. Chem. Soc.*, **59**, 241 (1937).

10) In this calculation n=1.8 was used and q assumed to be constant.

11) It can be accepted under the present experimental accuracy to reduce the ratio in kt by a factor of 2.

12) Such increase in Et with increasing conversion is also detected from the temperature dependence of kp/kt. The data of kp/kt at 52% conversion in Table 3 lead to give about 0.5 kcal./mole as the value of $(Ep\text{-}Et)$, where Ep is the activation energy of propagation. Using Matheson's datum (Ep=6.3 kcal./mole)[6a] the Et value at 52% conversion is estimated as about 5.8 kcal./mole, the value of which in good agreement with that estimated from the temperature dependence of V_{pL} or V_d at the same conversion.

13) Spencer and Williams, *J. Colloid Sci.*, **2**, 117 (1947).

14) P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1057 (1940).

15) P. R. E. J. Cowley and H. W. Melville, *Proc. Roy. Soc. London*, **A210**, 461 (1952); ibid., **A211**, 320 (1952); In the latter reference the kt value in the fused polymer at 167°C. was reported as 4×10^4 l. mol./sec. While Matheson reported 1.22×10^7 at 30°C. and 1.87×10^7 at 60°C. as the kt value at low conversion. Using Cowley's value (20 kcal.) of Et in the fused polymer and Matheson's value (2.8 kcal.(of Et in the initial stages, the kt_g/kt_0 value at 100% conversion is estimated as about 1.2×10^{-8} at 167°C. and about 4×10^{-8} at 30°C.

16) C. H. Bamford and A. D. Jenkins, *Proc. Ror. Soc. London*, **A216**, 515 (1953).

that the photo-polymer precipitated near room temperatures occluded the active ends of polymer radicals. Recently the present author has found that the effects of conversion on V_{pL}, V_d, k_t and n are extremely reduced by the addition of chain-transfer substance, such as *n*-butylmercaptan, to the polymerization system.[17] This result seems to throw a powerful datum on the verification of the above mechanism.

Summary

The usual photochemical method and the rotating sector technique have been used to study the effect of conversion on the termination mechanism in the polymerization of methyl methacrylate. The strong rate acceleration, the extreme increase in kinetic chain lifetime and some decreases in the overall activation energy and the reaction order of chain termination have been detected with increasing conversion of the reaction system. These results are in good agreement with those reported on styrene in the first paper of this series and with the available data on this polymerization. These results have been discussed under several assumptions and confirmed to be due to a large change in the termination mechanism, i. e., from the activation-controlled termination of polymer radicals in the initial stages to the predominant diffusion-controlled termination in the later stages.

The author wishes to express his hearty thanks to Dr. Shoji Shida of this Institute for his helpful advice and encouragement during the course of this work.

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17) Unpublished

LETTER

The Structures and Lower Electronic States of Cyclobutadiene

By Shoji Shida

(Received March 22, 1954)

Since the earliest times of the development of quantum chemistry, cyclobutadiene has been frequently studied from the theoretical standpoint together with benzene. The molecule is of special interest because of its peculiarities in many respects when compared with benzene. On its molecular structure Coulson[1] and Craig[2,3]* have supposed that the molecule, if it exists, should not be square as usually assumed but may be rectangular in form. Until now no quantitative work has been done about this problem or as to how the lower electronic states, especially the ground state, change their location in the energy level schema on varying the structure.

The present author has calculated the energy levels of all configurations arising from four π-molecular orbitals, assuming five different structures varying from the square (I) to the rectangle (V) having the normal

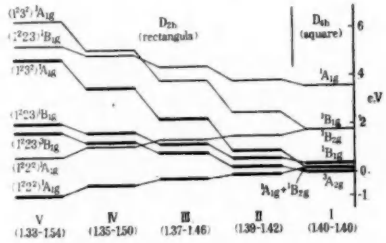

Fig. 1. The shifts of lower electronic states of cyclobutadiene with the changes of molecular dimensions.

Fine and thick stripes indicate the configuration energies computed by the ordinary ASMO method and by the method of atoms in molecules respectively. The $^3A_{2g}$ level in the square form (I) is taken as the reference state in both computations. (1.33–1.54), for instance, represents the short and long bond lengths in Å.

single and double bond lengths. The standard ASMO method without configuration

1) C. A. Coulson, private communication to the present author; C. A. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1947).
2) D. P. Craig, *Proc. Roy. Soc.*, **A 202**, 498 (1950).
3) D. P. Craig, *J. Chem. Soc.*, **1951**, 3175.
* And also the earlier work of J. E. Lennard-Jones and J. Turkevich, *Proc. Roy. Soc.*, **A 158**, 297 (1937).

interaction has been used at first. Next, to the results thus obtained has been added Moffitt's correction by the method of atoms in molecules.[4] Then the two sets of results have been compared. In the figure are shown the term values for only the lower energy states which are of primary importance for the present purpose. When comparing the ground state of (I) with that of (V) as obtained by the ASMO method, one might infer that the former would be more stable than the latter. On the other hand, according to the second treatment which seems to be more reliable, the lowest singlet level referred to the lowest triplet level is lowered throughout the five structures by 1.61 e. V. and the ground state of (V) is located about 0.9 e. V. below that of (I). The effect of configuration interaction has been known to be small, in general, in the method of atoms in molecules. To cite an example, in (I) the splitting (not shown in the figure) of degenerate $^1A_{1g}$ into $^1B_{1g}$ and $^1B_{2g}$ is only 0.3 e. V.[4,5] according to the method of atoms in molecules, whereas in the ordinary ASMO method it amounts to 3.5 e. V.[2] In the above, σ-bonds have been excluded from consideration; if these are taken into account the square form will still be unstable, because the energy gained in the modification process (V to I) of the σ-framework is relatively small (at most 3 kcal.). Now, it may safely be concluded that cyclobutadiene will not be stable in a square form and that, if it exists, it will take a rectangular form.

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The Crystal Structure of $Cs_3Fe_2Cl_9$ *and of* $Cs_3Sb_2Cl_9$

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A successful attempt has been made to obtain a new double chloride of cesium and ferric iron, which was expected to be isomorphous with $Cs_3Sb_2Cl_9$, and this compound as well as $Cs_3Sb_2Cl_9$ has been found to have the $Cs_3As_2Cl_9$ type of structure.

The double chloride $Cs_3Fe_2Cl_9$ was prepared by mixing solutions of cesium chloride and ferric chloride both in concentrated hydrochloric acid. The crystal of this compound was found under the microscope to be shaped like hexagonal plates and brownish orange in color, the larger crystals looking dark red to the naked eye. Under the polarizing microscope the crystal was found to be uniaxial. The crystal is stable if kept dry, but on exposure to moist air it is readily converted into the known double chloride $Cs_2FeCl_5 \cdot H_2O$. Accordingly, the accurate determination of density of this compound was not successful, but it was confirmed that this compound has a density higher than that of bromoform, 2.9.

It is known that the three arrangements $A_3B_2X_9$ are those typified by $Cs_3As_2Cl_9$,[1] $Cs_3Tl_2Cl_9$[2] and $Cs_3W_2Cl_9$[3]. Powder photographs of these three compounds as well as those of $Cs_3Fe_2Cl_9$ and $Cs_3Sb_2Cl_9$ were prepared, Cu K_α radiation ($\lambda = 1.542$Å) being used except in the case of $Cs_3Fe_2Cl_9$ in which Fe K_α radiation ($\lambda = 1.937$Å) was used. In order to avoid decomposition by atmospheric moisture during the preparation of the photograph, $Cs_3Fe_2Cl_9$ crystals were ground under the mother liquor, sealed together with the liquor in a thinwalled capillary of borosilicate glass of diameter 0.5mm., and then immersed in an X-ray beam. The similarity of $Cs_3Fe_2Cl_9$ and $Cs_3Sb_2Cl_9$ in the diffraction pattern suggested that the structure of these compounds belongs to the same type.

The cell dimensions derived are:

	a	c
$Cs_3Fe_2Cl_9$	7.28±0.05Å	8.90±0.05Å
$Cs_3Sb_2Cl_9$	7.61±0.05Å	9.32±0.05Å

The calculated densities are 3.37 and 3.41 respectively, with one formula unit per unit cell in each case. The observed intensities of reflection of $Cs_3Fe_2Cl_9$ and $Cs_3Sb_2Cl_9$ are well accounted for by means of the space group $D_{3d}^3 - P\bar{3}m1$, if the atomic positions are assumed as follows:

1Cs(1)	in	1(*a*) : 000
2Cs(2)	in	2(*d*) : 1/3 2/3 *z*, etc. with $z = 0.333$
2Fe(or Sb)	in	2(*d*) : 1/3 2/3 *z*, etc. with $z = -0.167$
3Cl(1)	in	3(*e*) : 1/2 0 0, etc.
6Cl(2)	in	6(*i*) : *xxz*, etc. with $x = 0.167$, $z = -0.333$

As was shown by Hoard and Goldstein[1] in their study on the structure of $Cs_3As_2Cl_9$, a slight distortion from the ideal structure adopted here would cause no essential change in the calculated intensities, but improve the agreement between the observed and calculated values a little.

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4) W. Moffitt and J. Scanlan, *Proc. Roy. Soc.*, **A220**, 530 (1953).
5) M. Wolfsberg, *J. Chem. Phys.*, **21**, 943 (1953).

1) J. L. Hoard and L. Goldstein, *J. Chem. Phys.*, **3**, 117 (1935).
2) J. L. Hoard and L. Goldstein, *J. Chem. Phys.*, **3**, 199 (1935). H. M. Powell and A. F. Wells, *J. Chem. Soc.*, **1935**, 1008.
3) C. Brosset, *Nature*, **135**, 874 (1935).